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CALCULATIONS AND DATABASING OF MOLECULAR ABSORPTION PARAMETERS FOR HITRAN

Robert R. Gamache

University of Lowell
Center for Atmospheric Research
Lowell, Massachusetts 01854

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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Total internal partition sums of the species on the HITRAN database are presented. The development of maintenance programs and update programs for the 1991 version of the HITRAN database is given and the construction of the 1991 version; new data and developments presented. The creation of new maintenance programs for updating halfwidths of O_3 and H_2O is discussed. Calculations are shown for the pressure broadened halfwidths of H_2O and CO_2 via several theoretical models. A summary of the 1991 HITRAN workshop is given with some recommendations for the future development.

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1.0 INTRODUCTION

This report summarizes work done in connection with the high-resolution transmission molecular absorption database HITRAN[1]. This database is a compilation of spectroscopic parameters from which one is able to calculate and predict the transmission and emission of radiation in the atmosphere. The work presented here spans a wide range of the problems one encounters when maintaining a database. In this report we discuss calculations of fundamental parameters needed by the database, calculations of data needed for application of the database to specific problems, the creation of maintenance and updating programs which help eliminate the many errors that can occur when dealing with large amounts of data, creating the newest version of the database, and we discuss the overall philosophy used in the development of the 1991 database.

In the second section, the work done in computing total internal partition sums for temperatures from 70 to 3000 K for the species on the HITRAN database and the fitting of this data to particular models is discussed. The total internal partition sums (TIPS) allows the application of the database to other temperatures as well as the calculation of the transition moment squared or Einstein coefficients. Section 3 gives the programming philosophy adopted for all programs that interact with the database. Various programs used for updating, maintenance, and producing the new versions are presented and the interrelationships between the programs shown. The fourth section describes the effort behind the 1991 version of the HITRAN database describing all differences one will observe between the 1986 version and the 1991 version as well as the structural changes made to the database. Section 5 discusses the calculation of pressure-broadening coefficients for various species on the database. The application of direct access files to create mixed databases of experimental and theoretical pressure-broadening coefficients for addition to HITRAN is discussed. Section 6 gives the relationships between the line intensities, transition squared, and the Einstein coefficient. Section 7 reviews the two workshops that were held on the HITRAN database and gives some of the views of the author. Finally section 8 gives some of the presentations and publications derived from this work.

2.0 TOTAL INTERNAL PARTITION SUMS

During the period of this contract the total internal partition sums (TIPS) were calculated for most of the isotopic variants on the database. This augmented some earlier work done for the principal atmospheric species. The total internal partition sum is given by

$$Q(T) = \sum_{\text{all levels}} (2J+1)\,(2S+1)\,(2-\delta_{\lambda 0})\,(g_n)\,e^{-E/kT} \quad , \qquad (1)$$

where

$(2J+1)$	J spatial degeneracy
$(2S+1)$	m_S spatial degeneracy
$(2-\delta_{\lambda 0})$	lamda doubling degeneracy
(g_n)	nuclear spin (state dependent and state independent) degeneracy
E	Total energy of the level, electronic, vibrational, and rotational.

The original intent was to extract quantum numbers and energies directly from the database and perform the sum in equation (1). It was realized that for many of the species on the database the resulting TIPS would not be converged at the elevated and even intermediate temperatures under consideration. Thus it was decided to calculate near complete sets of energy levels via the Hamiltonian of the species in question. Attempts would be made to go to high enough energy such that these terms in the sum [Eq. (1)] would have little to no effect on the final results.

Direct summation of equation (1) over all vibration-rotation levels was done whenever possible. For many of the species however, molecular constants are not available for all vibrational bands. The TIPS via a direct sum for this situation would have many energy levels missing and/or would have a cutoff in energy that is too low. For these cases it was assumed that the vibrational and rotational energies are separable and the partition sum can be written as a product of the vibrational partition sum and the ground state rotational partition sum,

$$Q(T) = Q_{vib}(T) \times Q_{rot}(T) \quad . \qquad (2)$$

The effect of a cutoff, Figure 1a, is to remove all energies above the cutoff value from entering into the sum. Applying a cutoff to the ground state and then applying the product approximation, $Q_{vib}(T) \cdot Q_{rot}(T)$, has the effect of including many energy levels above the ground state cutoff as shown in Figure 1b.

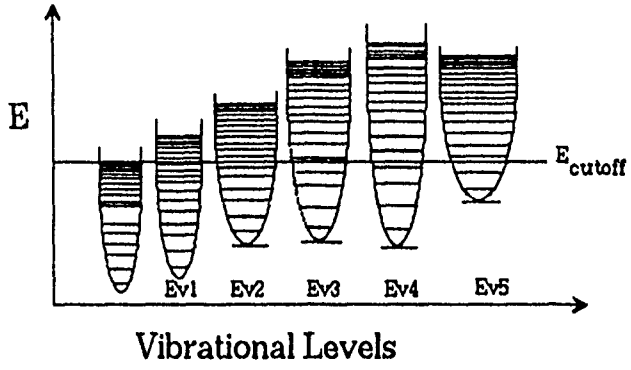

Figure 1a. Energy cutoff applied to ro-vibrational energy levels.

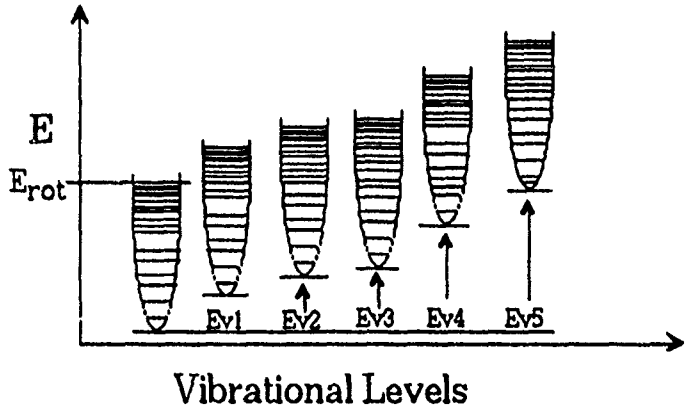

Figure 1b. Energy cutoff applied to ground state energy levels, followed by the product approximation.

When the product approximation was made both Q_{vib} and Q_{rot} were calculated by direct summation. In the calculations, the energies of the ground vibrational states were determined from the Hamiltonian for each species in question. The vibrational partition sums were calculated using the vibrational energies in the literature or in some cases estimated for lesser isotopic species. The vibrational sum is usually over 5 to 10 terms

and the rotational sum can be over several hundred to several thousand levels. The product approximation was shown[2] to be accurate to a few tenths of a percent for water vapor, carbon dioxide and ozone. When energy levels were not available for direct summation then the classical values were used.

The TIPS were to be calculated at a number of temperatures and these fit by different expressions. After some consideration we settled on fitting in three temperature ranges; 70-415K in 5K steps, 385-2005K in 20K steps, and by extrapolation of the 1900 and 2005K points to the 2005-3000K range.

Several representations for the temperature dependence of the total internal partition sums were tried by fitting to the data. The first expression used came from the work of McDowell[3] and had the form

$$Q_r \approx \sigma^* \pi^{1/2} c^{\beta/4} \beta^{-3/2} \left(1 + 15D/4\beta B\right) \qquad (3)$$

where $\beta = hcB/kT$ (B = rotational constant) and $\sigma^* = (2I_y+1)n/\sigma$ (I_y = nuclear spin of the Y nuclei, σ = classical symmetry number) and D = centrifugal distortion constant. In this expression σ, β, D and B were treated as adjustable constants.

A simple polynomial expression in temperature with four adjustable constants,

$$Q(T) = a + bT + cT^2 + dT^3 , \qquad (4)$$

was then studied.

There is another form that is sometimes used. This considers the natural logarithm of Q(T) vs, 1/temperature. Several points are stored and values at other temperature can be obtained from the formula

$$\ln (Q(T)) = \frac{a}{T} + b \qquad (5)$$

The constants a and b are obtained from the stored points. For example S. Clough uses this method in the FASCODE[4] program and H. Pickett uses it in

the JPL Catalogue[5].

Test were performed by fitting expressions (3) through (5) to Q(T) data and then recalculating Q(T) and comparing this to the original Q(T) data. The results show that the polynomial form, Eq. (4), for the partition sum gave the most accurate results and is the simplest for recalculation of Q(T). This was the form that was chosen to represent the partition sums.

The constants in equation (4), the a, b, c, and d coefficients, were obtained by least-squares min-max fitting prccedure. The fit in the 70-415K range was constrained to better than 1% error. The fitting errors are always better than 1/2%. The 385-2005K range was constrained to 1% error at 415K and allowed to float to 5% at 2005K. This is because the partition functions are less accurate at the high temperatures. This fitting procedure do: : not jeopardize the fit at low temperatures where Q(T) is accurate. The final high temperature range results vary from 1/2% at 415K to 4% at 2005K as the worst case.

For the high temperature extrapolation of the partition functions in the range 2005-3000K, the linear parts of several forms were considered. The linear part was chosen because of the poor extrapolation qualities of polynomial representations. The forms chosen were the form used by S. Clough[4] and H. Pickett[5]

$$\ln Q(T) = \frac{a_1}{T} + a_0 \qquad (6)$$

from Irwin[5]

$$\ln Q(T) = a_1 \ln(T) + a_0 \qquad (7)$$

and two classical (rotational) forms

$$Q(T) = a_1 T + a_0 \text{ and } \ln Q(T) = a_1 T + a_0 . \qquad (8)$$

To test the methods, the total internal partition sums were calculated for $H^{35}Cl$ from T = 2000 K to 3000 K in 100 K steps. For this species the energies were calculated to 44,500 cm^{-1} giving the TIPS an uncertainty of less than 2%. Using the coefficients previously obtained, the extrapolated

partition sums were calculated for each method and the % error with the direct sum computed. These values were plotted in Figure 2. Similar results were obtained for CO_2 and CO. All results indicate that expression (2) gives the best extrapolation of the methods tested.

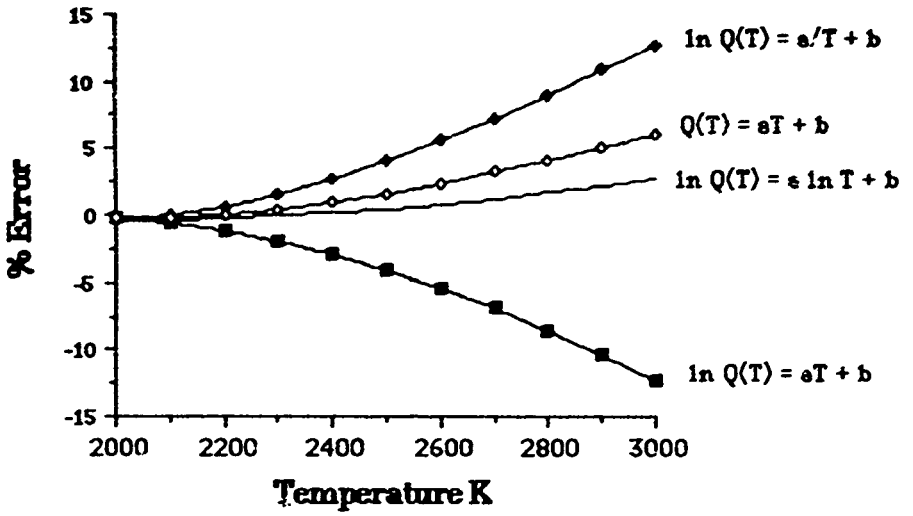

Figure 2. % Error from extrapolation methods vs. temperature

The remaining terms needed to evaluate equation (1) (once the energies are obtained) are the statistical factors. Some of these are dictated by the quantum numbers, thus they are state dependent. Others are independent of the particular vibrational-rotational state and are state independent factors and can be brought out of the summation in Eq. (1). Because these state independent factors are constant for a given species and usually ratios of the partition functions are used they are commonly omitted. The internal partition sums calculated in this work contain all terms explicitly. Thus they can be used to calculate thermodynamic functions, etc.

This includes nuclear statistical factors that are state independent. These terms arise from the nuclear statistics of nuclei that do not couple with the rotational wavefunctions because of symmetry. The nuclear statistical factor generates additional multiplying terms of $g_j = (2I+1)$ for each nuclei that is not coupled with the rotational wavefunctions, where I is the spin of the nucleus in question. These have been calculated and are given in Table 1.

Table 1. State Independent Nuclear Spin Degeneracy Factors

Molecule	AFGL Isotope Code	$g_j = \Pi(2I_j + 1)$	Molecule	AFGL Isotope Code	$g_j = \Pi(2I_j+1)$
H_2O	161	1	HNO_3	146	6
	181	1			
	171	6	OH	61	2
	162	6		81	2
				62	3
CO_2	626	1			
	636	2	HF	19	4
	628	1			
	627	6	HCl	15	8
	638	2		17	8
	637	12			
	828	1	HBr	19	8
	728	6		11	8
O_3	666	1	HI	17	12
	668	1			
	686	1	ClO	56	4
				76	4
N_2O	446	9			
	456	6	OCS	622	1
	546	6		624	1
	448	9		632	2
	447	54		822	1
CO	26	1	H_2CO	26	1
	36	2		136	2
	28	1		128	1
	27	6			
			HOCl	165	8
CH_4	211	1		167	8
	311	2			
	212	3	N_2	44	1*
O_2	66	1*	HCN	124	6
	68	1		134	12
	67	6		125	4

Table 1 continued

NO	46	3	CH_3Cl	215	4
	56	2		217	4
	48	3			
			H_2O_2	1661	4
SO_2	626	1			
	646	1	C_2H_2	1221	1*
				1231	8
NO_2	646	3			
			C_2H_6	1221	64
NH_3	4111	3			
	5111	2	PH_3	1111	2

* not applicable due to symmetry

2.1 Water Vapor, H_2O

For water vapor it is not possible to calculate all vibration-rotation energies beyond ≈ 7000 cm^{-1}, so we have calculated the total internal partition sums using the approximation $Q(T) = Q_{vib}(T) \cdot Q_{rot}(T)$. This has the effect of approximately including many of the high lying energy states that are removed when a cutoff is applied. The rotational partition sums were calculated with the Watson Hamiltonian constants of Flaud et al.[7] for $H_2{}^{16}O$, $H_2{}^{18}O$, and $H_2{}^{17}O$. The vibrational energies were taken from HITRAN to do a direct sum for the vibrational partition sum.

2.2 Carbon Dioxide, CO_2

For $^{12}C^{16}O_2$ the molecular constants of Wattson and Rothman[8] from the direct numerical diagonalization (DND) method were taken to generate the vibrational-rotational energy levels. This produced a set of energies complete to 16000 cm^{-1} with a cutoff of 20000 cm^{-1}. For $^{13}C^{16}O_2$ and $^{16}O^{12}C^{18}O$, the constants of Rothman et al.[9] were used, this generated energies up to 14055 cm^{-1} and 13860 cm^{-1} respectively. For these species direct summations were used to compute the TIPS.

For the other five less abundant species the energy levels were not available for all vibrational bands. For these species, $^{17}O^{12}C^{17}O$, $^{16}O^{13}C^{18}O$, $^{16}O^{13}C^{17}O$, $^{18}O^{12}C^{18}O$, $^{17}O^{12}C^{18}O$, the product approximation was employed

to evaluate the partition sums. The ground rotational parameters are from Chedin and Teffo[10]. The vibrational partition sums used the vibrational energies reported in Reference 1. The product $Q_{vib} * Q_{rot}$ was done to give the total internal partition sums for these species of CO_2.

2.3 Carbon Monoxide, CO

The energy levels of $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{12}C^{17}O$, and $^{13}C^{18}O$ were calculated using the Dunham expansion with the constants of Guelachvili et. al.[11]. The energies were calculated for v = 0 to 9 and J = 0 to 74. The range of v and J considered generated a complete set of energy levels to 10000. cm^{-1} and we expect the total partition sums will converge for all temperatures.

2.4 Monodeuterated Methane

For CH_3D the energy levels have not been calculated yet. To compute the total internal partition sum for this species we have taken the rotational partition sum from Robiette and Dang-Nhu[12] at 300 K, Q_{rot}=9095.0, and computed the temperature variation as

$$(Q(T)) = Q(300K) \times \left(\frac{T}{300}\right)^{1.5} . \qquad (9)$$

The vibrational partition sum was evaluated by direct summation of the vibrational energies given in HITRAN[1]. The total internal partition sum was then computed via $Q_{vib} \cdot Q_{rot}$.

2.5 Ammonia, NH_3

The energy expression for ammonia is given reference 13 with the inversion energy was calculated using the Padé approximation of Young and Young[14] The constants used for $^{14}NH_3$ are from Poynter and Margolis[13] with corrections to the constants C, D_K, H_K, and L_K from Cohen et.al.[15] The inversion energy constants were taken from reference 14. Symmetry rules for the allowed energy levels from Dowling[16] were used to

write an energy level program. With the program, energies were calculated for J = 0 to 50 (≈22000 cm^{-1})

The statistical factor, g_τ, for explicit rotational-inversion levels was taken from Bunker[17]. With these factors the rotational partition sums were calculated for the temperatures in question.

For $^{15}NH_3$ the symmetric and antisymmetric rotation-inversion constants were taken from Carlotti et. al.[18] with ν_0 for inversion from Sasada[19]. Energies were calculated for J = 0 to 50 (≈22000 cm^{-1}).

Vibrational energies were taken from subroutine MOLEC[20] (part of FASCODE[4]) to give the total internal partition sums for these species.

2.6 Sulfur Dioxide, SO_2

The energies of the ground vibrational state were calculated using the Watson Hamiltonian constants of Carlotti et al.[21] for the species $^{32}S^{16}O_2$ and the constants of Pine et al.[22] for the species $^{34}S^{16}O_2$. Calculations were done for J = 0 to 95 and levels up to ≈7000 cm^{-1} were retained. The vibrational partition sum used the vibrational energies from Reference 22. These are for the principal isotopic species only thus the sums for the $^{34}S^{16}O_2$ species will be more in error, however, this is expected to be very small. The rotational and vibrational partition sums were calculated and the product taken for the TIPS

2.7 Nitric Acid, HNO_3

For nitric acid, the Watson Hamiltonian constants that were used came from the work of Maki and Wells[23]. The calculation of the rotational energies considered J = 0 to 103 to produce some 10816 energy levels to ≈ 4500 cm^{-1}. The vibrational partition sum employed the vibrational energies published in the HITRAN paper[1] as compiled by Rinsland[24]. The total internal partition sum was calculated by the approximation, Qvib*Qrot.

2.8 Hydroxyl Radical, OH

The calculation of the energy levels followed the methodology of reference 25 for ^{16}OH, and reference 26 for ^{16}OD and ^{18}OH. The methods are a direct diagonalization of the three interacting states. The energies obtained from diagonalization were assigned as follows, the lowest belongs to the $^2\Pi_{3/2}$ state, the slightly higher value belongs to the $^2\Pi_{1/2}$ state, and the largest value is for the $^2\Sigma_{1/2}$ state.

A program was written to determine the energies by diagonalizing the matrices as a function of J, and F values for ^{16}OH via the formalism above[25]. The molecular constants used were from Goldman[27] for the H_{rot} and H_{SO} terms, from Coxon[28] for the hyperfine terms, and from Destombes[25] for the second order hyperfine terms. Energies E(J, F)were calculated for all F states of a given J for J = 1/2 to 74.5. This generated energies up to 6 $x10^4$.

For the other species, ^{18}OH and ^{16}OD, constants were not available from the literature for the same analysis. For these species the formalism of Beaudet and Poynter[26] was used. The formalism is similar to that of Destombes et. al. except all second order terms and higher are omitted. The Calculations were done for ^{16}OD and ^{18}OH for J equal to 1/2 to 74.5 (all F states). The rotational partition sums were then calculated for each species. The vibrational energies were calculated using

$$G_v = G_{v0} + w_e\left(v+\frac{1}{2}\right) - w_e x_e\left(v+\frac{1}{2}\right)^2 \qquad (10)$$

Constants for ^{16}OH are from Coxon[29] and for ^{16}OD from Coxon[30]. The constants for ^{18}OH were assumed the same as for ^{16}OH. The total internal partition sums were then calculated via the approximation $Q_{tot} = Q_{rot} * Q_{vib}$.

2.9 Hydrogen Bromide, HBr

The energy levels of this diatomic molecule were calculated using the Dunham expansion with the constants of Stocker and Goldman[31]. The energies were calculated for v = 0 to 9 and J = 0 to 74 which generates

energy levels to 43811. cm^{-1} thus the total partition sums will converge for all temperatures.

2.10 Hydrogen Iodide, HI

For HI, the energies were calculated by the Dunham expression using constants provided by R. Tipping[32]. The energies were calculated for v = 0 to 9 and J = 0 to 74 which generates energy levels to 31000. cm^{-1} and the total partition sums will converge for all temperatures.

2.11 Chlorine Monoxide, ClO

Chlorine monoxide is an inverted spin doublet with the $^2\Pi_{3/2}$ state being lower in energy than the $^2\Pi_{1/2}$ state. the energy levels were calculated by an effective Hamiltonian following Cohen et. al.[33]. The molecular constants for the rotational, hyperfine, and quadrupole interactions were taken from references 33-36. The rotational partition sums were calculated from these energy levels. The vibrational energies from reference 36 were taken to compute Qvib. The total internal partition sums were then calculated by the product approximation.

2.12 Carbonyl Sulfide, OCS

For OCS the rotational Hamiltonian constants are from Lovas[37]. Energy levels were calculated for each species from J = 0 to 200, this yields energies to ≈ 8000 cm^{-1}. The rotational partition sums were calculated from these energy levels. The vibrational partition sums were calculated using the vibrational energies from Ref 1. The total partition sums were done via the approximation $Q_{tot} = Q_{vib} * Q_{rot}$.

2.13 Formaldehyde, H_2CO

The rotational energies of the two species $H_2{}^{12}C^{16}O$ and $H_2{}^{13}C^{16}O$ were taken from Winnewisser et al.[38] Calculations considered levels from J = 0 to 75 and a 7000 cm^{-1} cutoff was applied to give energies for the

rotational partition sums. The rotational partition sums were then done for these two species. Watson constants have not yet been obtained for the $H_2{}^{12}C^{18}O$ species. The vibrational energies for the principal species are from reference 1. These were used to compute the total partition sums for this species.

The total internal partition sum for the $H^{13}C^{16}O$ species was calculated via the assumption

$$Q_{tot}(H_2^{13}C^{16}O) = Q_{vib}(H_2^{12}C^{16}O)*Q_{rot}(H_2^{13}C^{16}O). \qquad (11)$$

The reason for this assumption was that the vibrational energies of the $H^{13}C^{16}O$ species were not known. For $H_2{}^{12}C^{18}O$ there are no Watson Hamiltonian constants available for this isotopic species. For the time being the partition sum for this species has been assumed to equal that of the principal species $H_2{}^{12}C^{16}O$.

2.14 Hydrogen Hypochlorite, HOCl

For the vibrational energies, the HITRAN values were used for both isotopic species. The energy levels of HOCl were calculated using the Watson Hamiltonian constants of Wells, Sams, and Lafferty[39]. Some 5776 energy levels were generated for each isotopic species ($HO^{35}Cl$ and $HO^{37}Cl$) by calculating levels from J = 0 to 75 and cutting off at 7000 cm^{-1} to give 2326 $HO^{35}Cl$ lines and 2332 $HO^{37}Cl$ lines. The rotational partition sums were done by summing over these energy values with appropriate degeneracies. The final total sums were then calculated by the product formula.

2.15 Nitrogen, N_2

For the nitrogen molecule, the energies were calculated for all states from v = 0 to 9 and J = 0 to 75 via the Dunham expansion using the constants of Reuter et. al.[40] This gave all energy levels from 0 to ≈31000 cm^{-1}. The nuclear statistical factors came from Hertzberg[41]. For $^{14}N_2$ this gives g_s = 6 for the symmetric levels (J even) and g_s = 3 for the anti-

symmetric levels (J odd). The total internal partition sum was calculated by direct summation over all energies.

2.16 Hydrogen Cyanide, HCN

The constants for the three isotopic species considered for this molecule are from the work of Maki[42] with some updates from Lovas[37]. Calculation of levels from J = 0 to 75 were done for each species. This produced energies up to ≈ 8000 cm^{-1}. The rotational partition sums were calculated at the 150 temperatures using these energies. The vibrational energy levels are available for $H^{12}C^{14}N$ from HITRAN, for $H^{12}C^{15}N$ from Alpert, Mantz, and Rao[43], and for $H^{13}C^{14}N$ from reference 43 and scaling of the $H^{12}C^{14}N$ vibrational levels. The final TIPS were calculated via the product of $Q_{vib}*Q_{rot}$.

2.17 Hydrogen Peroxide, H_2O_2

Hydrogen peroxide is a light asymmetric rotor and it has substantial centrifugal distortion contributions to its rotational-torsional spectrum. The torsional states are fourfold degenerate, in the lowest torsional state (n=0) the fourfold degeneracy is broken and a doublet of doublets occurs. The four sublevels are designated by τ = 1, 2, 3, 4 in order of increasing energy. The τ = 1 and τ = 2 states and the τ = 3 and τ = 4 states are degenerate. The energy levels were calculated via ASMROT using the rotational-torsional constants of Helminger et. al.[44] for the τ=1,2 and τ=3,4 torsional states. Energies were calculated for J=0 to 35 (≈ 10000 cm^{-1}) and were used to calculate the ground state partition sum. The vibrational energies from MOLEC were used to produce the vibrational partition sums and the product taken for the total internal partition sums.

2.18 Acetylene, C_2H_2

For acetylene the molecular parameters for the two species are from Hietanen et. al.[45,46]. Energies were calculated up to J = 100 (12,000. cm-1) for the ground state of each species The ground state partition sums were

evaluated and for the principal species agree very well with the value given by McDowell[47] (at 100 K, Q(here) = 118.8487 and Q(McDowell) = 118.8263). The vibrational energies were from MOLEC. The total internal partition sums were done at the 150 temperatures of the grid used for fitting.

2.19 Phosphine, PH_3

The energy expression for PH_3 is given reference 48 .The inversion energy is negligible for PH_3 and was omitted. The molecular constants for PH_3 were taken from Maki et. al.[48]. Energies were calculated for J =0 to 75 (≈25000 cm^{-1}) from which the ground state partition sums were evaluated at the desired temperatures. The statistical factors, g_i's, are given in reference 49. Vibrational energies were taken from reference 1 to give the total internal partition sums.

3.0 PROGRAMMING

There were many programming tasks during this contract period. Many of the programs created were for one time use and were stand alone programs. However, there are many programs that are used often and interact with the evolution of the database. Some of these are maintenance programs for the database and others perform operation on the database and/or auxillary files. In order to create a set of maintenance programs that will remain compatible with the database now and in the future, a modular programming structure was adopted. The reason for this is that many of the programs use subroutines and data that are common to all, e.g. the vibrational state indices. If this information is updated in one program it must then be updated in all programs calling on that data. Unfortunately the editing of all programs containing the data is often overlooked. With the modular structure common information is kept in individual files consisting of one to several subroutines and a BLOCK DATA subroutine. When changes are made to the module, the module is compiled and the object code linked with the appropriate maintenance or operational programs. Figure 3 shows some of the interrelationships

between the modules and the maintenance and updating programs. (Unfortunately, other programs may also possess a dependence on these modules. An example is GENERATOR.FOR which creates the final set of CO_2 parameters and must be consistent with the vibrational indices chosen for the current edition of HITRAN.)

	BD-MOL	BD-VIBS	BD-ISO	BD-QT	BD-ABUN
SELECT91	✓	✓	✓	✓	
TR-MOM	✓	✓	✓	✓	✓
BSUM91	✓	✓	✓		
TIPS	✓		✓	✓	
MK-VIB	✓	✓	✓		
TCORR			✓	✓	
REMOVE91	✓	✓	✓		
FNDREF	✓	✓	✓		

Figure 3. Interrelationships between modules and programs.

3.1 Program SELECT

SELECT is the user-friendly interface to the HITRAN database. Its function is to allow users to remove from the database the portion of the transitions they require. Many changes have been made to the program SELECT to produce the new version SELECT91. These include; the coupling of a wavenumber/block correspondence table to decrease the time necessary to step ahead to the beginning wavenumber of the requested search; temperature dependent output files for a range of temperatures from 75 to 2005 K; a faster search procedure; an option to create batch run input file in the user-friendly mode,and input to the program has also been made easier and more fool-proof.

The wavenumber-block correspondence table has been used to improve speed of selection to up to a factor of ≈9 compared with the 1982 version. This is accomplished by the new file structure shown in figure 4. This structure allows very fast selection for all molecule, particular

molecule/all isotopes, and particular molecule/particular isotope searches. The increased speed is accomplished by writing a 1986 format file of the selected transitions and using the wavenumber-block correspondence table to quickly remove the transitions and encoding/decoding the minimum number of bytes in the data. This is shown in figure 5.

The time consuming encoding/decoding is only done when a user request other than the 1986 standard format. These formats are shown in figure 4 and constitute what are labeled file 3 (hard copy output) and file 4 (line file in another format or at a temperature other than 296 K). The encoding/decoding is only done on the selected lines saving a great deal of time.

The 1991 version of HITRAN has the wavenumber-block table in the first two blocks along with a version number that will link particular versions of HITRAN and SELECT. All changes will be downward compatible. This also implies that mismatching of SELECT and HITRAN versions will default to the slow selection mode.

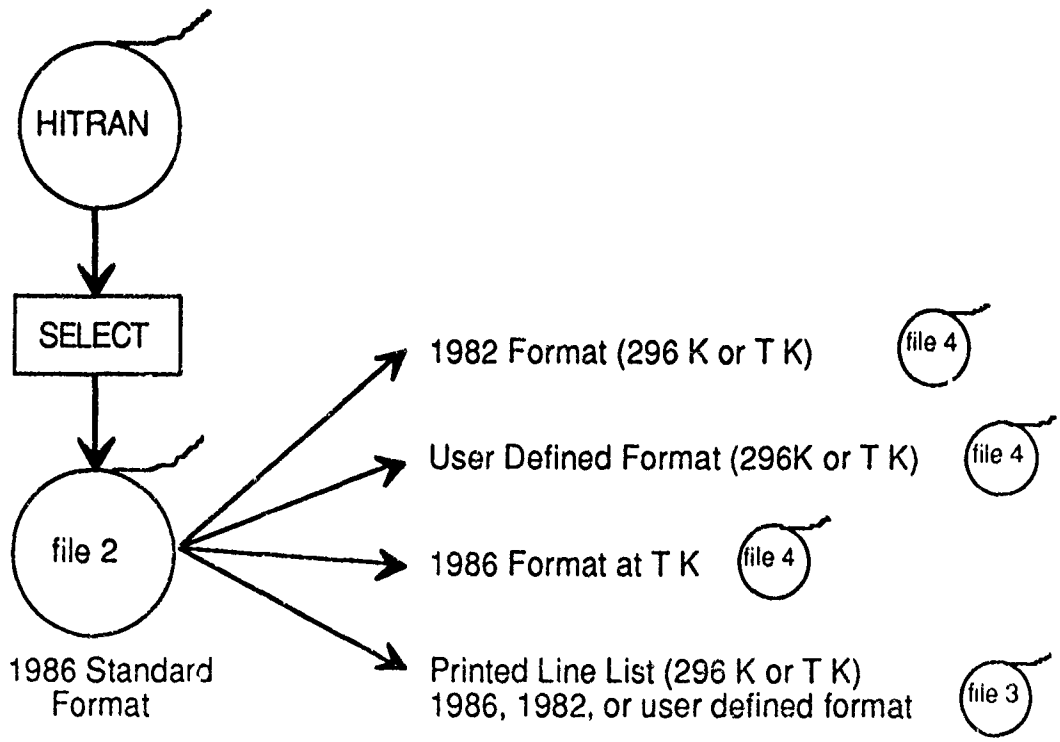

Figure 4 File structure for SELECT 1991

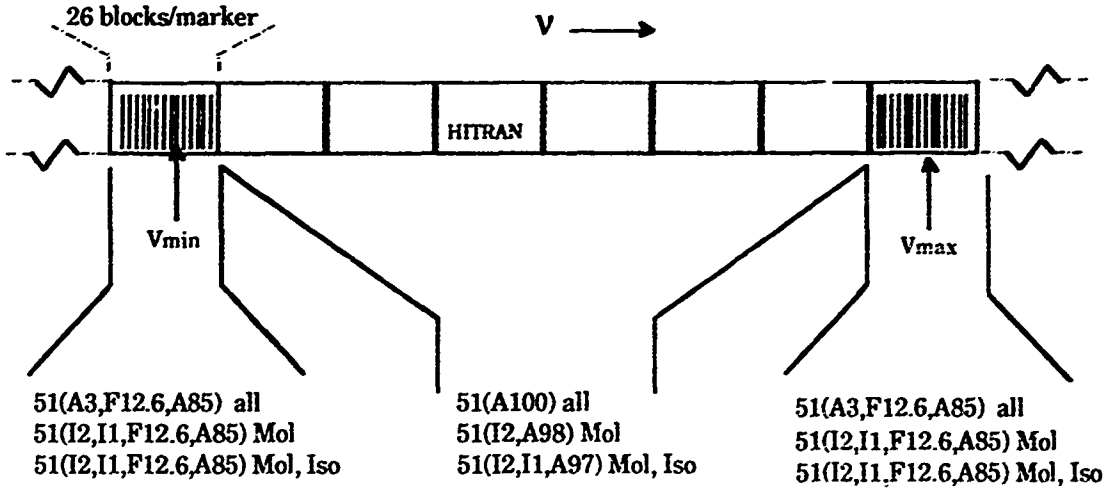

Figure 5. Fast read structure employing the wavenumber-block correspondence table.

The temperature dependent output option allows a user to generate a file of spectral data at temperatures other than 296° K. The current limitations are T = 70 to 3000° K. The corrections are to the line intensity and to the halfwidth at half-max via

$$S(T) = S(T_0)\frac{Q(T_0)}{Q(T)}e^{\left\{\frac{c_2 E''(T-T_0)}{T T_0}\right\}}\left[\frac{\left\{1-e^{-c_2\nu_{i,f}/T}\right\}}{\left\{1-e^{-c_2\nu_{i,f}/T_0}\right\}}\right] \qquad (12)$$

and

$$\gamma(T) = \gamma(T_0)\left(\frac{T_0}{T}\right)^n . \qquad (13)$$

The values of Q(T) are obtained from the polynomial coefficients given in BLOCK DATA and the values of n are given on HITRAN. For transitions where the TIPS are not yet available or the lower state energies are not on the database (unassigned lines) the lines are not written to the output file and a warning is issued to the user with some statistics about these lines.

The program SELECT91 has been thoroughly tested on the new database. The program can function with the 1986 database as well by defaulting to the general search and using the subroutine FASREAD to advance the database. This does make selections much slower. We have tested all the options and enhanced the user friendly aspects especially for avoiding errors. This version of SELECT91 is distributed as the first file on

3.2 Program TR-MOM

The 1986 HITRAN database saw the addition of the transition moment squared to the list of parameters for each spectral transition. At the time of the release of the 1986 edition we did not have a sufficient number of partition functions for all the species so the value used for the transition moment squared did not have the partition sums taken out. Since that time we have generated the partition sums for most of the species on the database and we are now able to compute the transition moment squared from the line intensity for most of the transitions on the database. In addition we have slightly modified the parameter on the database from the standard definition of the transition moment squared. This is to facilitate the use of the parameter for computation of Einstein coefficients. Thus, the 1991 edition of the HITRAN database has the field for the weighted transition moment squared implemented whenever possible.

The program that does this is TR-MOM. This reads a line in the 1986 HITRAN format, extracts the necessary information from the line, looks up the partition sums and degeneracy factors and calculates the weighted transition moment squared, $R_{\eta\eta'}$, given by

$$\frac{1}{d_\eta}\sum_{\xi,\xi'}|R_{(\eta\xi)(\eta'\xi')}|^2 = \frac{3hc}{8\pi^3}\,\frac{S_{(\eta)(\eta')}(T)}{\omega_{(\eta)(\eta')}\left(1-e^{hv_{(\eta\chi\eta')}/kT}\right)}\,\frac{Q(T)}{d_\eta\, e^{-E_\eta/kT}} \qquad (14)$$

The line is then written to an output file with the $R_{\eta\eta'}$. The relationships between $R_{\eta\eta'}$ and the Einstein coefficients is described in section 6.

3.3 Program BANDSUM91

We have written a new version of the bandsum program that fully makes use of the vibrational vector coding. This has allowed us to construct a very general program that can be run on the entire database of on individual files by simply changing the band center input selection list. The advantage here is that a version with smaller array dimensions can be

run on the PC for several molecules at a time. To run the program one must have a file of bands and band centers. From this list, vibrational vectors are constructed and stored. This list is compared to the vibrational state of each line on the database as a function of molecule and isotope so that the matches can be stored for each vibrational band of each isotopic species. The new bandsum program also does range checks for all parameters of the database thus allowing a greater checking of the consistency of the database.

3.4 Program TIPS

Program TIPS is a user friendly program that request input for Molecule, Isotope, and Temperature. The program uses the polynomial coefficients for the fits to the partition functions, equation (4) in two temperature ranges 70-400K and 400-2005K, or the coefficients of equations (5) are used when the temperature is between 2005 and 300K. The program is designed to use BD-QT.for, BD-MOL.for, BD-ISO.for, and can easily be adapted into the codes of other users to determine the partition functions.

3.5 AGENDA

The data base program to maintain the agenda was improved to produce the next version of HITRAN. AGENDA is a dBFile of all changes to be made to HITRAN. The file keeps track of the status and location of the new data.

The programs were modified to make the screens more clear for the previous options, ADD A RECORD or MODIFY EXISTING RECORD. In addition two new options were added to CUMENU.PRG, these are an option to DELETE RECORDS and VIEW RECORDS.

In the ADD A RECORD option we made the screen prompt the user for a molecule. If the entered molecule is not a species present on HITRAN a message is issued and the Enter molecule prompt issued again. When a correct molecule is entered a routine relates molecule name to the number in the HITRAN list. In this fashion the molecule name and number always agree in the new database. In all subsequent options the molecule name

and number can not be edited and thus remain consistent. The fields Frequency, Strength, HW-air, HW-self, Energy, Tdep-HW, Shift, and Use have all been changed to logicals. The status line has been increased in size. Also the record number of the record is displayed.

When modifying records after each modification control is no longer returned to the main menu, one enters the number of the next record to be modified. A negative value will return control to the main menu.

The DELETE RECORD option request a record number and the record is then displayed. The user is asked if this is the correct record, a Y will delete the record a N returns the user to the main menu. Records that have been deleted can still be viewed and edited. In the upper right hand corner of these records a message is given "Record is marked for DELETION". VIEW RECORDS simply displays record after record. A question, View next record? ENTER (Y/N) is displayed. The value Y steps ahead and the value N returns one to the main menu.

The new version of the AGENDA routine allows us to track changes to be made to HITRAN much more reliably.

3.6 Program MK-VIB

In preparing to produce the next version of HITRAN we tried to automate the procedure as much as possible. There are two main tasks, first to remove data that is to be replaced from the database and next to add the new and replacement data to the remaining lines. The difficulty is in designating the data to be removed. The unique specifier is the quantum numbers of the vibrational transition (entire bands are replaced not lines within a band) and the molecule and isotope designation. We have written a program that reads the new data and extracts all unique vibrational labels and automatically constructs a vibrational table data statement for each species. This table will then be used in a program to remove data from the database. The resulting line list will contain all transitions that are to be retained in the 1990 version of HITRAN. In order to do this all data of each molecule must be grouped together and the program MK-VIB run on each molecule. This generates the list of all vibrational transitions of each isotopic species of each molecule that are to be removed from HITRAN 86.

3.7 Program REMOVE90

This list of data to be removed is used in a program, REMOVE90, that will be run on HITRAN 86. For each species of each molecule data that will be updated is removed from the database. This program counts the number of lines removed and the number of lines retained for each isotopic species of each molecule. This allows a firm understanding of the changes made. The resulting line file contains all the lines on HITRAN 86 that are to be retained in the 1990 version. This file will then be merged with the data files of new and updated data to produce HITRAN 1990.

3.8 Program ABUN

A program was written to take the most recent[50] atomic isotopic abundances and calculate the molecular abundances for HITRAN. The program creates a table of abundances and also prepares a data statement for BD-ABUN.for. As new atomic abundances become available they can be added to ABUN and the program rerun to automatically update data files.

3.9 Program Tcorr

This program allows one to change the line intensity to correspond to another temperature. It reads a HITRAN format data file, and the user inputs the desired temperature of the output file.

3.10 Program MK-REF

This is a program that uses the isotopic species vector coding to store and list the reference codes from the database. This allows us to keep track of what reference numbers are used for each species on the database.

3.11 Module BD-MOL

The molecule chemical symbols are stored in a BLOCK DATA subroutine in array positions 0 to 32. Any and all changes to the list need only be done here.

3.12 Module BD-VIB

This contains several subroutines to initialize the vibrational vectors, and to go back and forth between spectroscopic notation and vector notation. The BLOCK DATA statement contains all spectroscopic vibrational codes used for all of the HITRAN species.

3.13 Module BD-ISO

This contains several subroutines to initialize the isotopic species vectors, and to go back and forth between the AFGL isotope code and the vector notation. The BLOCK DATA statement contains all AFGL isotopic species codes used for all of the HITRAN species.

3.14 Module BD-ABUN

This contains a data statement in a BLOCK DATA routine for the isotopic abundance of each molecular species on the database.

3.15 Module BD-QT

This is a BLOCK DATA subroutine that contains the polynomial coefficients for the three temperature ranges the partition sums were calculated for 70-400K, 400-2005K, and 2005-3000K. The partition sum for each isotopic species is stored at the reference temperature 296K. And the state dependent and independent degeneracy factors are stored.

4.0 1991 HITRAN

The work on the new data to the 1991 HITRAN is briefly summarized below. Some new species have been added to the HITRAN database. To keep track of these AGENDA has been modified to consider these. The new species are COF_2 (molecule # 29), SF_6 (molecule # 30), H_2S (molecule # 31), and HCOOH (molecule # 32). This allows us to track additions and updates for these species.

A fifth isotopic species for carbon monoxide was added to the 1991 database, $^{13}C^{18}O$. This has shifted the isotopic vector positioning. All programs using the isotopic vector structure and the BD-ISO routines were modified to account for this. The isotopic abundance program was modified and the new abundances created. These are given in Table 2 with the appropriate number of significant figures.

4.1 H_2O

Water vapor has seen some significant improvements for this edition of the database. We have added the data of Flaud et al.[51-53] for the regions 8036-9482 cm^{-1}, 9603-11481cm^{-1}, and 13238-22657 cm^{-1}, the data of Toth[54,55] was used for the 5904-12741 cm^{-1} region and for the v2 region. The line count for these files is 1874, 2484, 4608, 3637, and 4618 lines respectively. For both of the Toth files strong lines were not included so they had to be taken from the 1986 database. This is discussed below. In general for this data we had to perform the following task

1. Reformat the data to the HITRAN86 format.
2. Convert line intensities from cm^{-2} atm^{-1} units to cm^{-1}/molec cm^{-2}.
3. Convert line intensities to 300° K to reference temp (296° K).
4. Add the intensity error codes.
5. Add the lower state energies for each line.
6. Add reference codes.
7. Add halfwidths and temperature exponents
8. Add lower state energies.

Table 2. Isotopic Abundances for Species on HITRAN91

Molecule	HITRAN isotope code	Abundance	Molecule	HITRAN isotope code	Abundance
H_2O	161	.997317	HF	19	.99984425
	181	.00199983			
	171	.000372	HCl	15	.757587
	162	.00031069		17	.242257
CO_2	626	.98420	HBr	19	.50678
	636	.01106		11	.49306
	628	.0039471			
	627	.000734	HI	17	.99984425
	638	.00004434			
	637	.00000825	ClO	56	.75591
	828	.0000039573		76	.24172
	728	.00000147			
			OCS	622	.93739
O_3	666	.992901		624	.04158
	668	.00398194		632	.01053
	686	.00199097		822	.0018797
N_2O	446	.990333	H_2CO	126	.98624
	456	.0036409		136	.01108
	546	.0036409		128	.0019776
	448	.00198582			
	447	.000369	HOCl	165	.75579
				167	.24168
CO	26	.98654			
	36	.01108	N_2	44	.9926874
	28	.0019782			
	27	.000368	HCN	124	.98511
	38	.00002222		134	.01107
				125	.0036217
CH_4	211	.98827			
	311	.01110	CH_3Cl	215	.74894
	212	.00061575		217	.23949
O_2	66	.995262	H_2O_2	1661	.994952
	68	.00399141			
	67	.000742	C_2H_2	1221	.97760
				1231	.02197
NO	46	.993974			
	56	.0036543	C_2H_6	1221	.97699
	48	.00199312			
			PH_3	1111	.99953283
SO_2	626	.94568			
	646	.04195	COF_2	269	.98654

Table 2. continued

NO_2	646	.991616	SF_6	29	.95018
NH_3	4111	.9958715	H_2S	121	.94988
	5111	.0036613			
			HCOOH	126	.98390
HNO_3	146	.989110			
OH	61	.997473			
	81	.00200014			
	62	.00015537			

Dr. Brown[56] informed us that the near-IR and visible data have many of the strong lines missing due to saturation. The same was found in the ν_2 region data from Toth. To alleviate this problem data for the following bands were extracted from the 1986 HITRAN, (010)-(000), (040)-(000), (120)-(000), (021)-(000), (200)-(000), (101)-(000), (002)-(000), (131)-(000), (310)-(000), (211)-(000), (112)-(000), and (013)-(000). This data were compared to that of Toth and all lines not present in the Toth data were retained. This gave us 2307 lines in the near-IR region, 669 lines in the visible region, and 86 lines for the ν_2 region that will be added to the 1991 database to complete the data for these bands.

4.2 CO_2

Dr. Laurence Rothman created a file containing all CO_2 lines. This file has the most up to date halfwidths, and temperature exponents, error codes, references and transition moments.

4.3 O_3

Permission was granted by Academic Press to use the ozone data of Flaud et al.[57] on the 1990 version of HITRAN. Curt Rinsland of NASA Langley sent us the complete data for ozone in six compressed files. The format of the files is a modified 1982 format. I wrote a program to reformat the data into the 1986 format, add the self and air-broadened halfwidths, the temperature dependence of γ, add the error code for γ, and to add data to the reference code as requested by Academic Press. Rinsland suggested not adding position and intensity error codes at this

time. The pure rotation data has only 4 significant figures after the decimal whereas we allow for 6. He suggest using the new file due to the improvements in the intensities and commented that the four significant figures was already more than the data could support.

The reformatting program was run on all the files. The reformatted files were merged in one file called OZONE.90 which contained 168881 lines. Inspection of the data statement revealed the ozone data would be a complete replacement of ozone data on HITRAN 86. The new data now contains 66 bands for the principal species and 5 bands each for the lesser isotopic species.

4.4 CO

The carbon monoxide files were obtained from R. Tipping[58]. There are 5 files, one for each isotopic species. Error codes and reference codes were added to the files. The data are in the files CO51.91, CO52,91, CO53.91, CO54.91, and CO55.91 and they contain 800, 700, 700, 700, and 700 lines respectively.

4.5 CH_4

All of the methane on the database was replaced with a file sent to us by Linda Brown[56].

4.6 NO

John Ballard's measurements[59] of the NO fundamental will be added to the database. Ballard has 12[illegible] from P 13.5 to R 19.5. The fundamental was extracted from the 1986 database to get the line missing in Ballard's data. Of the 417 lines from HITRAN 1986, there were 289 lines retained. The error and reference codes were set to zeros for these lines.

4.7 HNO_3

There are six files for HNO_3 from Aaron Goldman[50]. These lines are in the HITRAN format. The only change needed was the addition of the references. The data are in the files HNO3N2.91, HNO3N6.91, HNO3N7.91, HNO3N8.91, HNO3N9.91, and HNO3N89.91 and they contain 32340, 8379, 8013, 7101, 8091, and 9709 lines respectively.

4.8 Hydrogen Halides

Six files were obtained from R. Tipping[57] for the hydrogen halides, one each for HF and HI and two each for HCl and HBr. The references and error codes were added. The HCl files Tipping sent were in WORDSTAR format and had to be converted to text. One of these files had a decimal point in the wrong field indicating that all or part of the data was entered by hand(This may haunt us in the future). The final files for this data are HF.91, HCl151.91, HCl152.91, HBr61.91, HBr62.91, and HI.91 and they contain 107, 203, 168, 200, 198, and 237 lines respectively.

4.9 N_2

For nitrogen the data from HITRAN 86 was extracted and the intensities scaled by 1.049 and the halfwidth set to 0.047 cm^{-1}/atm as recommended by Curt Rinsland[61]. Reference codes were added to make the final file of 117 lines called N2.91.

4.10 H_2O_2

The ν_6 band was obtained from John Hillman[62] to replace the data on HITRAN 86. The file was reformatted and the shift and self-broadened halfwidth were set to 0, γ_{air} set to 0.10 cm^{-1}/atm, n=0.5, and reference codes added. The final file is H_2O_2.91 and contains 4561 lines.

4.11 C_2H_2

We have 119 lines of data for the ν_5 band of C_2H_2[61], this is new to the database. The error codes appeared to be in the style of the old date code (288) meaning February 1988. This was changed to 000. Reference codes were added and the final file is C_2H_2.91.

4.12 C_2H_6

This is the ν_7 band of C_2H_6[63], it is new data to HITRAN. There are 421 lines of data. Reference codes were added to the data. The data are in the file C_2H_6.91.

4.13 COF_2

This is a new molecule to the database. It has been assigned as molecule 29 and the isotope code is 1 corresponding to the GL code of 269, shorthand for $^{12}C^{16}O^{19}F_2$. There are three files for the ν_2, ν_4 , and ν_6 bands from Goldman et al.[64] and they contain 7234, 3250, and 7758 lines respectively.

4.14 SF_6

This is a new molecule to the database. It has been assigned as module 30 and the isotope code 1 corresponds to the GL code 29, short hand for $^{32}S^{19}F_6$. The data is from L. Brown[56] and is for the ν_3 band. These are a total of 11520 lines for this data.

4.15 Reference Codes

Reference codes have been implemented for all the new and updated data for the 1991 edition of HITRAN. To label data from the previous version the error and reference codes have all been set to zeros. This will indicate the reference of Rothman et al.[1]. A file of the references will be one of the files distributed with the HITRAN database. The 1991 edition of HITRAN will have both the error and reference codes fully active for the first time.

4.16 1986 HITRAN Data for the 1991 Edition

From a careful inspection of the AGENDA output listing we have determined which molecular species will be updated in the 1991 edition of HITRAN. A procedure has been developed to remove from the 1986 database all the data corresponding to the new data. This will leave behind all the 1986 data that will be retained in the 1991 edition. For the molecules CO_2, O_3, CO, CH_4, and the hydrogen halides all data is to be replaced thus these lines are simply removed from the 1986 database. For the other species to be updated, H_2O, NO, HNO_3, N_2, H_2O_2, C_2H_2, and C_2H_6 the following procedure was used. For each species all data was grouped into one file. The file was then run through MK-VIB which finds all unique vibrational bands in the data and creates a data statement of the vectorized transitions for each isotopic species, e.g. for water vapor the ν_2 transition is given by (010)-(000), the vector code is 2 to 1 and the vectorized transition is given by 1000*IVUP+IVLO thus for ν_2 we have 2001. This generates a data statement of all vibrational bands for each isotopic species of a molecule that must be removed from the 1986 database. **Nothing** must be typed by hand in this procedure. The data statements for each species were then put into a program REMOVE91 which was run on the 1986 database. The line counts from this procedure are given in Table 3 and they agree exactly with what one would expect from AGENDA.

Table 3 Line Counts from REMOVE91

Mol	Iso	retained	removed	Mol	Iso	retained	removed
H_2O	161	12098	17268	HNO_3	146	28496	7492
	181	5076	1039				
	171	2662	754	OH	61	8521	0
	162	8305	0		81	65	0
					62	90	0
CO_2	626	0	26201				
	636	0	8766	HF	19	0	62
	628	0	13046				
	627	0	6624	HCl	15	0	103
	638	0	2322		17	0	97
	637	0	1585				
	828	0	722	HBr	19	0	128
	728	0	288		11	0	128
O_3	666	0	47938	HI	17	0	145
	668	0	1149				
	686	0	993	ClO	56	3011	0
					76	.3009	0
N_2O	446	17792	0				
	456	1876	0	OCS	622	461	0
	546	1901	0		624	99	0
	448	1774	0		632	93	0
	447	782	0		822	84	0
CO	26	0	266	H_2CO	126	1772	0
	36	0	137		136	563	0
	28	0	111		128	367	0
	27	0	60				
				HOCl	165	8057	0
CH_4	211	0	14587		167	7508	0
	311	0	1130				
	212	0	2057	N_2	44	0	117

Table 3 continued							
O_2	66	1132	0	HCN	124	703	0
	68	612	0		134	34	0
	67	510	0		125	35	0
NO	45	5590	417	CH_3Cl	215	3977	0
	56	699	0		217	2710	0
	48	679					
				H_2O_2	1661	883	2389
SO_2	626	23372	0				
	646	287	0	C_2H_2	1221	1052	0
					1231	87	0
NO_2	646	20067	0				
				C_2H_6	1221	4328	0
NH_3	4111	4856	0				
	5111	961	0	PH_3	1111	2886	0

4.17 Structure of Cross-Section Files on HITRAN

The structure of the cross-sectional files on HITRAN had never been fixed to a precise format. For the 1991 version we have decided to use the following format; each file will start with a 100 byte header which contains the **chemical symbol** right justified in A10 format, the **initial wavenumber** and **final wavenumber** each in f10.4 format, the **number of points** of data in I10 , the **temperature** (in Kelvins) **and pressure** (in atmospheres) corresponding to the data in F10.4, the **Maximum cross-section** in the data in E10.3, and **source** of the data with comments in A30. The cross-sections corresponding to this header follows immediately in 100 byte lines (10E10.3) at a wavenumber spacing defined by

$$\Delta\nu = (\nu_{final} - \nu_{initial})/N_{points} \qquad (15)$$

The cross-sections and the X_{max} are in units of $cm^{-1}/(molec \cdot cm^{-2})$ at the temperature T. If the data ends in the middle of a line, the line is zero filled to the end. See Figure 6 for details. The next group of cross-section data begins on the next line with the header. This file will be put on HITRAN 91 in blocked form, 5100 bytes/block. This means that many of the cross-section records will begin within the block structure as shown in Figure 6.

4.18 The 1991 edition of the HITRAN Database

It should be noted that several iterations took place to produce the 1991 edition of the HITRAN database. Errors that were detected in the data were corrected. This included among other corrections; the HCl data from Tipping, addition of other data for NO_2, OCS, SF_6, and HNO_3, resetting reference codes for the Camy-Peyret et al. visible region H_2O data, NO_2 duplicate lines, etc. Each time an iteration was done we had to recreate the blocked database with the lookup vectors. This was tedious, required running several programs, and files had to be created and deleted during the process. To make the task more efficient, the programs were consolidated into one called MAKE_BLOCKED_HITRAN.for. To run this, one first must sort the unblocked HITRAN line file. This must be done by defining scratch working files by issuing the following commands on the VAX,

```
$ASSIGN SCRATCH SORTWORK0
$ASSIGN SCRATCH SORTWORK1
.                                                    .
                                                     .
                                                     .
                                                     .
                                                     .
$ASSIGN SCRATCH SORTWORK9
SORT/STABLE/KEY=(POS:4,SIZE:12)/WORK_FILES=10 filein fileout.
```

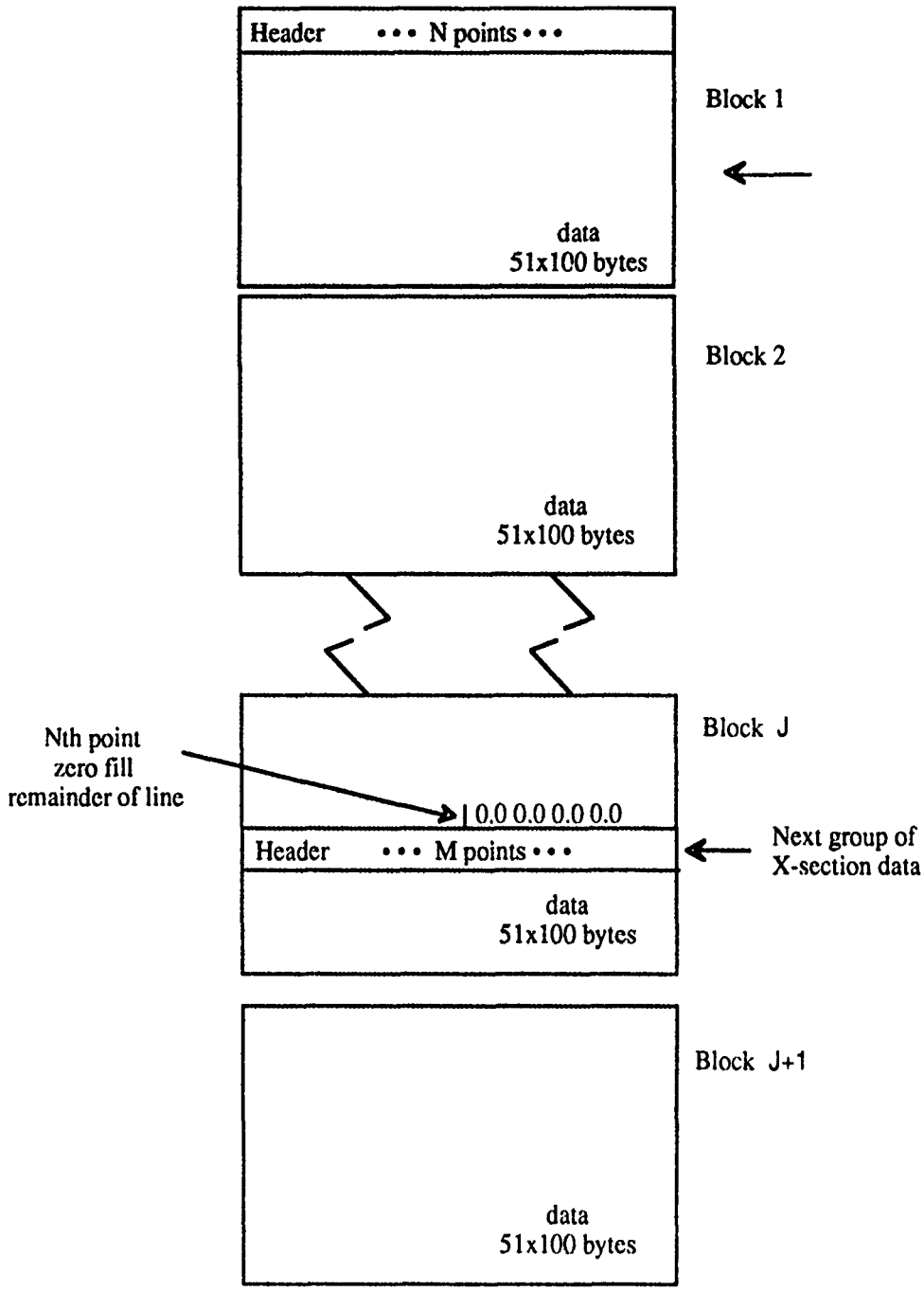

Figure 6. Structure of the 1991 Cross-section Files.

MAKE_BLOCKED_HITRAN then takes the sorted output file and blocks it into a scratch file(HITRAN format), the file is rewound and the frequency-block table is produced. From this file the frequency-block correspondence table is created, currently this puts 26 blocks per marker, and the edition number is entered and the correspondence blocks created

(there are two such blocks). Finally, the correspondence blocks and the blocked HITRAN file are written to one file, the new edition of the HITRAN database. The final database we created was labeled HITRAN Edition 03 1991 and it contains 647672 lines in total. In addition there are 102 = 2x51 "lines" of header and position pairs. Table 4 gives the line count for each isotopic species on the database.

New on this database is the use of the reference fields for the position, intensity, and air-broadening coefficient. We have made full use of these fields for all the new data and have set the remaining 1986 database lines to have a reference code of 0 for each parameter. In the new data we have also tried to implement the error codes whenever possible. The error codes for the 1991 database are given in Table 5 for the position and in Table 6 for the line intensity and the halfwidth.

5.0 BROADENING COEFFICIENTS

Much work was done in the area of the broadening coefficients for the 1991 database. This involved both calculations and better use of the experimentally measured values for several of the species on the database.

5.1 Air-Broadened Halfwidths for Water Vapor on HITRAN

Dr. Curtis Rinsland of NASA Langley sent a preprint[65] on measurements of air-broadened halfwidths of water vapor he made with Aaron Goldman, Mary Ann Smith, and Malathy Devi. I reviewed the preprint and was surprised by the agreement (or lack of agreement) between the HITRAN values and their measurements. I knew there would be differences but I did not expect them to be so large. When the calculations were done, 1979-80, there were not many measurements to compare with. For example, comparison made at that time for $J<8$ pure rotation lines gave an average absolute percent difference of 12.2 for some 14 lines. I think the differences found in the paper of Rinsland et al. are understandable given the nature of the work done in 1980.

Table 4 Line Count for HITRAN91

Mol	Iso	# transitions	Mol	Iso	# transitions
H_2O	161	48523	HNO_3	146	143021
	181	6357			
	171	3744	OH	61	8521
	162	8305		81	65
				62	90
CO_2	626	26887			
	636	8892	HF	19	107
	628	13343			
	627	6625	HCl	15	203
	638	2312		17	168
	637	1584			
	828	721	HBr	19	200
	728	288		11	198
O_3	666	142221	HI	17	237
	668	19147			
	686	7513	ClO	56	3011
				76	3009
N_2O	446	17792			
	456	1876	OCS	622	461
	546	1901		624	99
	448	1774		632	93
	447	782		822	84
CO	26	800	H_2CO	126	1772
	36	700		136	563
	28	700		128	367
	27	700			
	38	700	HOCl	165	8057
				167	7508
CH_4	211	35588			
	311	4926	N_2	44	117
	212	6457			
			HCN	124	703
O_2	66	1132		134	34
	68	612		125	35
	67	510			
			CH_3Cl	215	3977
NO	46	6007		217	2710
	56	699			
	48	679	H_2O_2	1661	5444
SO_2	626	23372	C_2H_2	1221	1172
	646	287		1231	86
NO_2	646	26296	C_2H_6	1221	4749
NH_3	4111	4856	PH_3	1111	2886
	5111	961			
			COF_2	269	18242
			SF_6	29	11520

Table 5. Error Code for the Wavenumber

Code	Error Range
0	≥ 1./ or undefined
1	≥ .1 and < 1.
2	≥ .01 and < .1
3	≥ .001 and < .01
4	≥ .0001 and < .001
5	≥ .00001 and < .0001
6	< .00001

Table 6. Error Code for the Line Intensity and Halfwidth

Code	Error Range
0	Undefined
1	Default or Constant
2	Average or Estimate
3	≥ .20%
4	≥ 10% and < 20%
5	≥ 5% and < 10%
6	≥ 2% and < 5%
7	≥ 1% and < 2%
8	<1%

The values presented on HITRAN are from two sources. One is the database of N_2-broadened halfwidths presented in the Applied Optics article[66] and the others are from an averaging algorithm devised by Dick Davies[67]. The calculations followed the work of reference 68. These calculations only considered the dipole (H_2O) - quadrupole (N_2) interaction and hence will be too small because the quadrupole (H_2O) - quadrupole (N_2) interaction has been omitted. In Davies' work the QFT scaling parameter α was set to 2.79 to match a calibration line (5 2 3→6 1 6) and the parameter b_{min} set to 1.5 Å. We have since found α = 2.50 to be a better choice. At the time, Davies was trying to adjust the theory to

explain some very narrow line widths for high J lines that were measured. This was accomplished by the low value of b_{min}. As stated by Davies and Oli[68], this choice of b_{min} may give questionable results for intermediate J values. This is what is observed. Note Benedict and Calfee[69] used a b_{min} value of 3.2 Å thus there results will be proportionally larger. It appears that the optimization of the calculations for the high J lines has led to halfwidths that are consistently low as shown by the results of Rinsland et al.. The other quantities that enter into the calculation, energies, reduced dipole and quadrupole line strengths, etc. were also not as well known for the intermediate to upper states of water vapor leading to more uncertainty in these calculations.

We did a few calculations to compare with Tables I and IV of reference 65. The calculations are essentially the method used in the 1988 paper on temperature dependence by Gamache and Rothman[70] and is nearly equivalent to that of Tejwani[71]. In ref. 70 the Tipping trajectory model[72] was used and Tejwani uses that of Robert and Bonamy[73]. It was shown for ozone[74] that these differ by 3% with the Tipping model giving the larger values. The calculations done here are somewhat larger than Tejwani's and without knowing the explicit molecular constants he used we cannot address the differences. What is more important is that although there appears to be agreement for these lines for the other pure rotational transitions studied there remains large differences. For one of the measured lines (6 2 5→7 5 2) we had done a QFT-ID (quantum Fourier Transform Theory with Improved Dynamics) calculation some years ago and the agreement is somewhat better than the BKG-ID value. Comparing with the 14 experimental lines mentioned above the QFT-ID method gave an average absolute percent difference of 7.7. However as higher J states are considered the agreement becomes worse. Clearly work in needed on comparing and developing the theories and the intermolecular potentials.

5.1.1 Direct Access Files for H_2O and O_3 halfwidths

For the updating of halfwidths on the database for O_3 and H_2O a new approach was developed. This is the use of direct access files on the PCs or the VAX to update the halfwidths. The approach is similar to the mass storage approach that was used on the CYBER however it is done on the PC

or VAX with much greater control. We have created direct access files of N_2 and self broadened halfwidths of H_2O which will run in ADHWH2O. From my calculations I have obtained the average halfwidth as a function of J which has also been added. These are given in Table 7.

Table 7. Average N_2- and Self-Broadened Halfwidths of H_2O

J''	γ_{N_2}	a	γ_{air}	a
0	.10554	1	.51760	1
1	.11038	7	.53498	7
2	.10532	19	.53558	19
3	.09897	33	.51965	33
4	.09217	47	.48387	47
5	.08512	61	.44795	61
6	.07762	75	.41578	75
7	.07016	89	.36937	89
8	.06319	103	.32831	103
9	.05690	117	.30085	117
10	.05139	131	.28184	131
11	.04650	145	.26001	145
12	.04199	159	.23730	159
13	.03787	173	.21433	173
14	.03405	187	.19057	187
15	.03038	201	.17076	201
16	.02701	215	.15836	215
17	.02405	229	.14736	229
18	.02277	208	.14874	208
19	.02045	226	.13518	226
20	.01856	156	.12327	156

For ozone I took the database of theoretical values[75] and stored these in a direct access file. The program to add the halfwidths operates as follows: given an initial and final state the DAF is searched for data. If available the N_2-broadened value is used. When there is no calculation

and J"<40 the averaged theoretical halfwidth is used. For these cases, the value is then scaled by 0.95 to get the corresponding air-broadened value. It is then scaled another 9% based on M. Smith's comparison[76] of the calculations to experiment. For air-broadening above J"=40 Curt Rinsland's polynomial values[77] are used. For the self-broadened values the polynomial expression of Smith et al.[78] determined by a fit to 355 measurements is used.

The addition of air- and self-broadened halfwidths and temperature exponents for H_2O has undergone a major change. The previous approach used a database of calculated values which are known to be in error especially for the intermediate J lines. The new approach uses experimentally determined halfwidths whenever possible. The procedure is as follows: for each perturber a master file was created consisting of the vibrational and rotational quantum numbers, the halfwidth, the error in the halfwidth, the shift, and a reference number. These files are used as input to a program to create the direct access files (DAFs) for γ and n. Currently the DAFs of halfwidths contain the value of the halfwidth, its error code and reference; the DAFs of temperature exponents contain n and the reference.. In creating direct access files the experimental data are given preference. When no experimental data exist scaled calculated values of Gamache and Davies[79] are used. The scaling values were determined separately for each broadening gas by comparing the theoretical and experimental values. From this analysis scale factors as a function of J were determined for both perturbers. The master files of the halfwidths can be updated at any time and the new DAF created.

5.2 Collision Broadened Halfwidths for CO_2

Rosenmann et al.[80,81] have computed the collision broadened halfwidths and temperature dependence for CO_2 perturbed by CO_2, H_2O, N_2, and O_2. This data was taken and used in a subroutine to evaluate the halfwidth for gaseous mixtures and temperature exponent for the temperature dependence of the halfwidth for CO_2 lines. This will be added to the CO_2 line generator program of Rothman to evaluate air-broadened halfwidths and the temperature exponent. Although it is a consistent set of data we have found it to be greater than the experimental results of

Johns[82] and Dana et al.[83] for all values of m. We have addressed the assumption of replacing the velocity integral by the mean relative thermal velocity, MRTV, as a possible cause for the differences. This approximation becomes more suspect at elevated temperatures. The reason for this is that at elevated temperatures the Maxwell-Boltzmann distribution of velocities spreads out and the assumption of replacing the integral over velocities by the mean relative thermal velocity is less valid. From our calculations we have found that the agreement is better at elevated temperatures. We have sought to explain this and have found some interesting results.

The Baranger-Kolb-Griem formalism[84] gives the Lorentz component halfwidth at half maximum (HWHM), γ_{if}, of isolated lines as the real part of the diagonal matrix elements of the resolvent operator. Within the impact approximation, the broadening coefficient is given by

$$\gamma_{if}(cm^{-1}/atm) = \frac{n}{2\pi c}\sum_{J_2}\rho_{J_2}\int_0^\infty v\, f(v)\, dv \int_0^\infty 2\pi b\, S_{if}(b,v,J_2)\, db \quad , \qquad (16)$$

where N is the number density of perturbers, v the relative velocity of the colliding pair, b is the impact parameter, c the speed of light, ρ_{J2} is the Boltzmann factor for the perturber state J_2, $f(v)$ is the Maxwell-Boltzmann velocity distribution function, and $S_{if}(b,v,J_2)$ has been called the collision efficiency function or the diffusion operator. It is found that by replacing the velocity integral by the mean relative thermal velocity and evaluating the diffusion operator at $\bar{v}$, gives results generally within 5-10% of that calculated by Eq(16). The the broadening coefficient in terms of the mean relative thermal velocity, $\bar{v}$, is given by

$$\gamma_{if}(cm^{-1}/atm) = \frac{n}{2\pi c}\sum_{J_2}\rho_{J_2}\,\bar{v}\int_0^\infty 2\pi b\, S_{if}(b,\bar{v},J_2)\, db \quad . \qquad (17)$$

Formally this expression is developed by assuming that $S_{if}(b, v, J_2)$ does not depend on velocity, thus allowing the integral on velocity to be done analytically. However the diffusion operator is known to vary with

velocity. The reason equation (17) is used in place of (16) is the savings in time for the calculation.

The need for broadening coefficients with an uncertainty of less than 10% has prompted us to study the approximation leading to Eq. (17). We have investigated the velocity dependence of $S_{if}(b, v, J_2)$ for CO_2 perturbed by N_2, O_2, and CO_2 and found that the agreement between values calculated via equations (16) and (17) is fortuitous and conclude that formally the velocity integral should be explicitly evaluated. Given this, we have recalculated the halfwidths and temperature exponents for N_2, O_2, and CO_2 broadening of CO_2 by explicitly using equation (16).

We have compared these values to the calculations of Rosenmann et. al.[80,81]. In general we find that from |m| up to 20 our calculations are lower than Rosenmann's, bringing them closer to the experimental values. The reason for the lowering is that the MRTV calculations have an artificial resonance in the diffusion operator from ≈ 5 x10-8 to 7 x10^{-8} cm. This can be seen in figure 7 for the J"=1 R-branch transition of CO_2 interacting with the J_2=0 level of N_2 at 296K. At |m|=20 the curves cross and our calculations are lower than Rosenmann's by 3% at |m|=25 decreasing to 0.5% for |m|>100. It should be emphasized that the MRTV calculations even when they agree with the full calculation do so only by a fortuitous cancellation of errors. Differences in the interruption functions approaching 90% (Figure 8) have been observed between the two methods.

6.0 LINE INTENSITY, TRANSITION MOMENT SQUARED, EINSTEIN COEFFICIENTS, AND OSCILLATOR STRENGTHS

The 1986 HITRAN database saw the addition of the transition moment squared to the list of parameters for each spectral transition. At the time of the release of the 1986 edition we did not have a sufficient number of partition functions for all the species so the value used for the transition moment squared did not have the partition sums taken out. Since that time we have generated the partition sums for most of the species on the database and we are now able to compute the transition

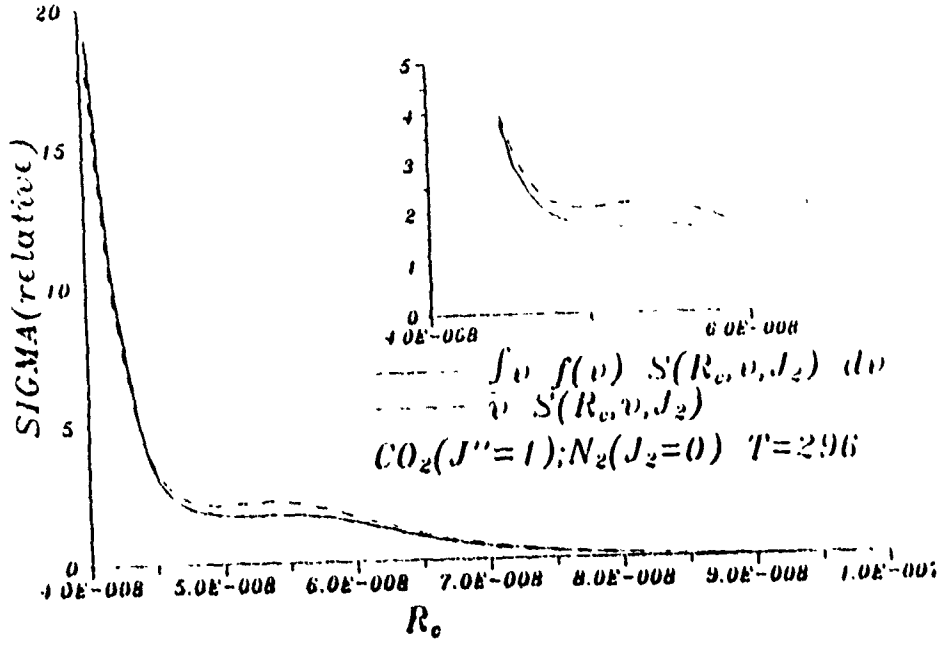

Figure 7. Comparison of diffusion operator calculated from equations (16) and (17) for CO_2(J"=1) R transition perturbed by J=0 level of N_2.

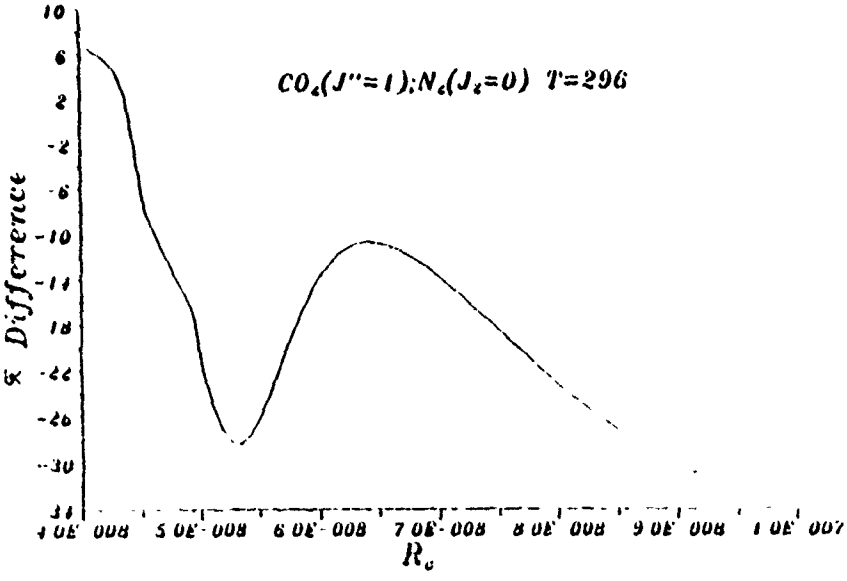

Figure 8. Percent difference between diffusion operator calculated from equations (16) and (17) for CO_2(J"=1) R transition perturbed by J=0 level of N_2.

moment squared from the line intensity for most of the transitions on the database. In addition we have slightly modified the parameter on the database from the standard definition of the transition moment squared. This is to facilitate the use of the parameter for computation of Einstein coefficients. Below we describe the relationships between the line intensity, Einstein coefficients, transition moments and oscillator strengths.

We start by defining the number of molecules per unit volume in quantum states l (lower state labeled by vibration, rotation quantum numbers n,J,M) and u (upper state n',J',M')

$$N_l = \frac{N g_l e^{-E_l/kT}}{Q}, \qquad N_u = \frac{N g_u e^{-E_u/kT}}{Q}, \tag{18}$$

where N is the total number of molecules per unit volume, g_l and g_u are the degeneracies of states l and u respectively, and Q is the total internal partition function. We consider isotropic space and non degenerate levels at first and later generalize to the degenerate case. The Einstein coefficients are

$B_{l\to u}$ Einstein coefficient for induced absorption

$B_{u\to l}$ Einstein coefficient for induced emission

$A_{u\to l}$ Einstein coefficient for spontaneous emission.

The number of transitions per unit time per unit volume from state l to u is

$$N_l B_{l\to u} \rho_{\nu_{lu}} - N_u B_{u\to l} \rho_{\nu_{lu}} \tag{19}$$

and the number of transitions per unit time per unit volume from state u to l is

$$N_u A_{u\to l} . \tag{20}$$

At equilibrium there is a balance

$$N_l B_{l\to u} \rho_{\nu_{lu}} = N_u \left(B_{u\to l} \rho_{\nu_{lu}} + A_{u\to l} \right) . \tag{21}$$

Rearranging equation (21) gives

$$\frac{N_l}{N_u} = \frac{B_{u\to l}\rho_{\nu_{lu}} + A_{u\to l}}{B_{l\to u}\rho_{\nu_{lu}}} \qquad (22)$$

which is well known from Boltzmann statistics

$$\frac{N_l}{N_u} = \frac{Ng_l e^{-E_l/kT}\, Q^{-1}}{Ng_u e^{-E_u/kT}\, Q^{-1}} = \frac{g_l}{g_u} e^{-h\nu_{lu}/kT} \qquad (23)$$

Combining equations (22) and (23) yields

$$\rho_{\nu_{lu}} = \frac{A_{u\to l}/B_{u\to l}}{\frac{g_l}{g_u}\left(\frac{B_{l\to u}}{B_{u\to l}}\right)e^{-h\nu_{lu}/kT} - 1} \qquad (24)$$

Comparing this with the Planck function,

$$\rho_{\nu_{lu}} = \frac{8\pi h\nu_{lu}^3}{c^3}\frac{1}{e^{-h\nu_{lu}/kT} - 1}, \qquad (25)$$

gives

$$A_{u\to l} = \frac{8\pi h\nu_{lu}^3}{c^3} B_{u\to l} \qquad (26)$$

and

$$g_l B_{l\to u} = g_u B_{u\to l} \qquad (27)$$

The integrated absorption coefficient can be written

$$S_{lu} = \int_{\Delta\nu_{lu}} k_{L,\nu} d\nu = \left(N_l B_{l\to u} - N_u B_{u\to l}\right)\frac{h\nu_{lu}}{c}, \qquad (28)$$

and using Eq. (27) gives

$$S'_{lu} = N_l B_{l\to u}\left(1 - \frac{N_u g_l}{N_l g_u}\right)\frac{h\nu_{lu}}{c} \quad , \tag{29}$$

or from Eq. (26) we find

$$S'_{lu} = \frac{c^2}{8\pi\nu_{lu}^2} N_l A_{u\to l}\left(1 - \frac{N_u g_l}{N_l g_u}\right) \quad . \tag{30}$$

At thermal equilibrium we have from equation (6) $N_u g_l / N_l g_u = \exp(-h\nu_{lu}/kT)$ and equations (29) and (30) become

$$S'_{lu} = N_l B_{l\to u}\left(1 - e^{h\nu_{lu}/kT}\right)\frac{h\nu_{lu}}{c} \tag{31}$$

and

$$S'_{lu} = \frac{c^2}{8\pi\nu_{lu}^2} N_l A_{u\to l}\frac{g_u}{g_l}\left(1 - e^{h\nu_{lu}/kT}\right) \quad . \tag{32}$$

The quantity S'_{lu} represents the integral of the spectral absorption coefficient over effective width $\Delta\nu_{lu}$ of the spectral line whose center is at ν_{lu}. It has dimensions of $cm^{-1}sec^{-1}$ and is referred to as the integrated absorption. It practice one uses a spectral absorption coefficient in $cm^{-1}atm^{-1}$ given by S'_{lu}/pc (p in atms)

$$S_{lu} = \frac{S'_{lu}}{pc} = \frac{h\nu_{lu}}{c}\frac{1}{pc} N_l B_{l\to u}\left(1 - e^{h\nu_{lu}/kT}\right) \tag{33}$$

or

$$S_{lu} = \frac{S'_{lu}}{pc} = \frac{c}{8\pi\nu_{lu}^2}\frac{N_l}{c} A_{u\to l}\frac{g_u}{g_l}\left(1 - e^{h\nu_{lu}/kT}\right) \quad . \tag{34}$$

We now wish to relate this to the transition moment squared. From Penner[85] we find the transition moment squared is related to the probability that in unit time a system will undergo a transition from a state n to a state m under the influence of an external field of volume density $\rho_{\nu mn}$ where $E_m > E_n$ by

$$\frac{c_m^* c_m}{t} = \frac{2\pi}{3h^2} |R_{mn}|^2 \nu_{mn} \quad . \tag{35}$$

Relating $m \rightarrow u$ and $n \rightarrow l$ the probability of a transition is also given by

$$\frac{c_m^* c_m}{t} = B_{l \rightarrow u} \rho_{\nu_{ul}} \quad . \tag{36}$$

From equations (26), (27), (35), and (36) we find

$$B_{l \rightarrow u} = \frac{8\pi^2}{3h^2} |R_{ul}|^2 \quad , \tag{37}$$

$$B_{u \rightarrow l} = \frac{8\pi^3}{3h^2} \frac{g_l}{g_u} |R_{ul}|^2 \quad , \tag{38}$$

and

$$A_{u \rightarrow l} = \frac{64\pi^4}{3hc^3} \frac{g_l}{g_u} \nu_{ul}^3 |R_{ul}|^2 \quad . \tag{39}$$

Finally, from equations (33) and (37), or (34) and (39) we find

$$S_{lu} = \frac{8\pi^3}{3hc^2} \frac{N_l}{p} \nu_{lu} \left(1 - e^{h\nu_{lu}/kT}\right) |R_{lu}|^2 \tag{40}$$

or with $\nu_{lu}/c = \omega_{lu}$

$$S_{lu} = \frac{8\pi^3}{3hc} \frac{N_l}{p} \omega_{lu} \left(1 - e^{h\nu_{lu}/kT}\right) |R_{lu}|^2 \quad . \tag{40a}$$

Equations (40) relate the line intensity, S_{lu}, to the transition moment squared, $|R_{lu}|^2$, for the non degenerate case.

The dimensionless absorption oscillator strength $f_{l\rightarrow u}$ is defined through the relation

$$S'_{lu} = \frac{\pi e^2}{mc} N_l f_{l\rightarrow u}\left(1 - e^{h\nu_{lu}/kT}\right), \tag{41}$$

where e and m denote, respectively, the electronic charge (in esu) and the mass (in gm/electron). Hence the integrated absorption and dimensionless *f*-number are related through the expression

$$S_{lu} = \frac{\pi e^2}{mc^2} \frac{N_l}{p} f_{l\rightarrow u}\left(1 - e^{h\nu_{lu}/kT}\right). \tag{42}$$

The emission oscillator strength $f_{u\rightarrow l}$ is related to $f_{l\rightarrow u}$ through the expression

$$f_{u\rightarrow l} = -\frac{g_l}{g_u} f_{l\rightarrow u}. \tag{43}$$

From equations (37), (40a), and (42) we can relate the absorption oscillator strength, the transition moment squared, and the Einstein coefficient for induced absorption

$$f_{l\rightarrow u} = \frac{8mc}{3he^2} \omega_{lu} |R_{lu}|^2 = \frac{2hmc}{\pi^2 e^2} \omega_{lu} B_{l\rightarrow u}. \tag{44}$$

Relationships with the other Einstein coefficients can be easily obtained from Eqs. (38) and (39).

States are usually degenerate and we must add this complication to the formulas. For example, evaluation of the number of molecules in a particular state from Boltzmann statistics in the most general case is

$$N_i = \frac{Nd_i e^{-E_i/kT}}{Q} = \frac{Ng_i g_j (2J+1)(2S+1)(2-\delta_{0\Lambda}) e^{-E_i/kT}}{Q} \tag{45}$$

where d_i is the degeneracy of state i given by the coupling of the nuclear spins with the rotational wave functions, g_i, the state independent nuclear spin factors, $g_j=\Pi_k(2I_k+1)$, the M degeneracy, (2J+1), the spin degeneracy, (2S+1), and lamda doubling $(2-\delta_{0\Lambda})$, and Q is the total internal partition function.

Let us start by considering a simple case with M degeneracy only. The formulas derived so far apply to the non degenerate case thus we can write the following expressions for the non-degenerate sublevels:

$$A_{(nJM)(n'JM')} = \frac{64\pi^4}{3hc^3}\, \nu^3_{(nJM)(n'JM')} \left|R_{(nJM)(n'JM')}\right|^2 . \qquad (46)$$

The integrated absorption for the non-degenerate case is then

$$S_{(nJM)(n'JM')} = \frac{c}{8\pi\nu_{lu}^2}\frac{N_l}{p} A_{(nJM)(n'JM')}\left(1-e^{h\nu_{lu}/kT}\right)$$
$$= \frac{8\pi^3}{3hc}\frac{N_{nJM}}{p}\omega_{(nJM)(n'J'M')}\left(1-e^{h\nu_{(nJM)(n'J'M')}/kT}\right)\left|R_{(nJM)(n'JM')}\right|^2 . \qquad (47)$$

However in the absence of an electric or magnetic field, the levels are degenerate with degeneracies $g_{nJ} = (2J+1)$ for the lower state and $g_{nJ'} = (2J'+1)$ for the upper state. For transitions between the degenerate energy levels $E_{n'J'}$ and E_{nJ}, the fundamental expression for the Einstein coefficient for spontaneous emission becomes

$$A_{(nJ)(n'J)} = \frac{1}{g_{n'J'}} \sum_{M,M'} A_{(nJM)(n'J'M')} , \qquad (48)$$

where the summation extends over all allowed values of M and M' that are consistent with the specified energy transition. Equation (48) follows from the fact that, in the absence of a radiation field, the Einstein coefficient is defined in such a way that

$$-\frac{dN_{nJM}}{dt} = N_{nJM}\, A_{(nJM)(n'J'M')} = \frac{N_{nJ}}{g_{nJ}} A_{(nJM)(n'J'M')} , \qquad (49)$$

whence

$$-\frac{dN_{n'J'}}{dt} = \sum_{M,M'} \frac{-dN_{n'JM'}}{dt} = \frac{N_{n'J'}}{g_{n'J'}} \sum_{M,M'} A_{(nJM)(n'JM')} \quad . \qquad (50)$$

Equations (49) and (50) show that $N_{n'J'} = N_{n'J'M'} \cdot (2J'+1)$, i.e. (2J+1) times other degeneracies. Using (46), equation (48) can be rewritten for the degenerate levels

$$A_{(nJ)(n'J')} = \frac{1}{g_{n'J'}} \nu^3_{(nJ)(n'J')} \sum_{M,M'} \frac{64\pi^4}{3hc^3} \left|R_{(nJM)(n'J'M')}\right|^2 \quad . \qquad (51)$$

Using (47) for non-degenerate energy levels along with (48) we find that

$$S_{(nJ)(n'J)} = \sum_{M,M'} S_{(nJM)(n'JM')} \qquad (52)$$

or

$$S_{(nJ)(n'J)} = \frac{8\pi^3}{3hc} \frac{N_{nJ}}{p} \omega_{(nJ)(n'J)} \left(1 - e^{h\nu_{(nJ)(n'J')}/kT}\right) \frac{1}{g_{nJ}} \sum_{M,M'} \left|R_{(nJM)(n'JM')}\right|^2 \quad . (53)$$

We now consider the general situation where the lower and upper states may have several types of degeneracy, for example a state may have M degeneracy from the various projections of J on a space fixed axis and a degeneracy from the coupling of nuclear spins with the rotational wavefunctions. The quantum numbers labeling the states can be divided into two sets; one set for the non-degenerate labels, η, and the other set labeling the degeneracies, ζ. To illustrate this, above we have been considering the vibration-rotation state labeled by n,J,M. In this labeling scheme the non-degenerate set of quantum numbers ,η , is n and J, and the degenerate set, ζ, is the M's. The energy of the state is labeled by η and the number of molecules in each state is given by

$$N_\eta = \frac{N d_\eta e^{-E_\eta/kT}}{Q} \quad . \tag{54}$$

The Einstein coefficient for spontaneous emission is defined from

$$-\frac{dN_{\eta'\xi'}}{dt} = N_{\eta'\xi'} A_{(\eta\xi)(\eta'\xi')} = \frac{N_{\eta'}}{d_{\eta'}} \sum_{\xi,\xi'} A_{(\eta\xi)(\eta'\xi')} \quad , \tag{55}$$

and

$$-\frac{dN_\eta}{dt} = \sum_{\xi,\xi'} \frac{-dN_{\eta'\xi'}}{dt} = \frac{N_{\eta'}}{d_{\eta'}} \sum_{\xi,\xi'} A_{(\eta\xi)(\eta'\xi')} \quad , \tag{56}$$

where the summation extends over all allowed values of ζ,ζ' that are consistent with the specified energy transition. Again we note that $N_\eta = d_\eta \cdot N_{\eta\zeta}$ The Einstein coefficient for spontaneous emission becomes

$$A_{(\eta)(\eta')} = \frac{1}{d_{\eta'}} \sum_{\xi,\xi'} A_{(\eta\xi)(\eta'\xi')} \quad , \tag{57}$$

or

$$A_{\eta'\to\eta} = \frac{64\pi^4}{3h} \omega^3 \frac{1}{d_{\eta'}} \sum_{\xi,\xi'} |R_{(\eta\xi)(\eta'\xi')}|^2 \quad . \tag{58}$$

We also have

$$B_{\eta'\to\eta} = \frac{8\pi^3}{3h^2} \frac{1}{d_{\eta'}} \sum_{\xi,\xi'} |R_{(\eta\xi)(\eta'\xi')}|^2 \quad , \tag{59}$$

and

$$B_{\eta\to\eta'} = \frac{8\pi^3}{3h^2} \frac{1}{d_\eta} \sum_{\xi,\xi'} |R_{(\eta\xi)(\eta'\xi')}|^2 \quad . \tag{60}$$

In this notation the line intensity is related to the transition moment squared by

$$S_{(\eta)(\eta')} = \frac{8\pi^3}{3hc}\,\frac{N_\eta}{p}\,\omega_{(\eta)(\eta')}\left(1-e^{hv_{(\eta)(\eta')}/kT}\right)\frac{1}{d_\eta}\sum_{\xi,\xi'}\left|R_{(\eta\xi)(\eta'\xi')}\right|^2 \quad . \qquad (61)$$

Using equations (54) and (61) we find the following

$$\frac{1}{d_\eta}\sum_{\xi,\xi'}\left|R_{(\eta\xi)(\eta'\xi')}\right|^2 = \frac{3hc\ p}{8\pi^3}\,\frac{S_{(\eta)(\eta')}(T)}{\omega_{(\eta)(\eta')}\left(1-e^{hv_{(\eta)(\eta')}/kT}\right)}\,\frac{Q(T)}{Nd_\eta\ e^{-E_\eta/kT}} \qquad (62)$$

where $S_{(\eta)(\eta')}$ has units of cm^{-1}/atm. Rewriting (62) in HITRAN units of $cm^{-1}/(molecules \cdot cm^{-2})$ p and N are absorbed into S to get

$$\frac{1}{d_\eta}\sum_{\xi,\xi'}\left|R_{(\eta\xi)(\eta'\xi')}\right|^2 = \frac{3hc}{8\pi^3}\,\frac{S_{(\eta)(\eta')}(T)}{\omega_{(\eta)(\eta')}\left(1-e^{hv_{(\eta)(\eta')}/kT}\right)}\,\frac{Q(T)}{d_\eta\ e^{-E_\eta/kT}} \quad . \qquad (63)$$

This is the quantity that has been added to the database in the transition moment squared field we will call the weighted transition moment squared. This is more useful to those wanting Einstein coefficients since this is just $3h^2/2\pi$ times $B_{l\rightarrow u}$.

The program TR-MOM.for reads each line in HITRAN format and, depending on the molecule, decodes the necessary information (quantum numbers etc.) for the degeneracy calculation, calculates the total internal partition sum (TIPS), and then computes the weighted transition moment squared, R^2. The line is then written to a file with this additional information. TR-MOM has been run on all the lines in the 1991 HITRAN database. For molecules for which we do not have the TIPS a zero is written for the R^2.

There are several advantages to the definition Eq. (63). First, it removes from the partition functions the degeneracy of the state η. This is important in that our partition functions were calculated with all the degeneracy factors accounted for. Thus our Q(T) could be used to calculate thermodynamic quantities. In spectroscopic applications, the state independent degeneracy factors (e.g. non-coupled nuclear spin) are often left out. Had we not removed the factor of d_η from the partition sum, the transition moment squared on the database would have carried these

factors. This could have caused many problems to the users. Another reason is that $R_{\eta\eta'}$, as we define it, is $3h^2/2\pi$ times the Einstein coefficient for induced absorption.

The transition moment squared can be expressed in terms of the matrix elements of the various j components of the dipole moment by

$$|R_{(nJM)(n'JM')}|_j = \left(\psi^*_{nJM}\left|\mu'_j(r,\Theta,\phi)\right|\psi_{n'J'M'}\right), \tag{64}$$

where n, J, and M, denote, respectively, the vibrational, rotational, and magnetic quantum numbers; $\mu'_j(r,\theta,\phi)$ is the effective j^{th} component of the electric dipole moment vector $\mu(r,\theta,\phi)$ and $\Psi_{n,J,M}$ stands for the complete time-independent wave function of the molecule. We assume separability of the wave function in the form

$$\psi_{nJM} = S_{nJ}(r)\ g_{JM}(\theta,\phi), \quad g_{JM}(\theta,\phi) = \Phi_M(\phi)\ \Theta_J^{|M|}(\theta), \tag{65}$$

the j^{th} component of the dipole moment μ'_j may be written as

$$\mu'_j(r,\theta,\phi) = \mu(r)\ f_j(\theta,\phi), \tag{66}$$

with $\mu(r)$ given by

$$\mu = \sum_i \mu_i (r-r_e)^i \tag{67}$$

The transition moment squared can now be written

$$\frac{1}{d_{nJ}} \sum_{M,\,M'} |R_{(nJM)(n'JM')}|^2 = \left|S^*_{nJM}|\mu(r)|S_{n'J'}\right|^2 \frac{1}{d_{nJ}} \sum_{M,\,M'} \sum_j \left|g^*_{J,M}\,|f_j(\theta,\phi)|\,g_{J',M'}\right|^2 \tag{68}$$

For molecules with vanishing electronic angular momentum, the double sum appearing in the preceding expression is the reduced dipole moment matrix element for the rotational transition from state J to J'

$$\frac{1}{d_{nJ}} \sum_{M,M'} \sum_{j} \left| g^{*}_{J,M} \left| f_j(\theta,\phi) \right| g_{J',M'} \right|^2 = \langle J \| \mu \| J' \rangle^2 \quad . \tag{69}$$

These matrix elements obey the sum rule

$$\sum_{J'} \langle J \| \mu \| J' \rangle^2 = 1 \quad . \tag{70}$$

The square of the vibration-rotation matrix element is denoted by

$$\left| M_{n,Jn'J'} \right|^2 = \left| S^{*}_{n,} \left| \mu(r) \right| S_{n'J'} \right|^2 \quad , \tag{71}$$

and it follows that with the definition of the weighted transition moment squared given by Eq. (63) and if the vibration-rotation matrix element has little J dependence we have

$$\sum_{J'} R^2_{n,Jn'J'} \frac{1}{\left| M_{0,0} \right|^2} \approx 1 \quad . \tag{72}$$

The rotational states, J' , to sum over in equation (72) are determined by the selections rules for the particular molecule under consideration.

The sum rule given by Eq. (72) allows us to perform checks on the line intensities and weighted transition moment squared for bands on the database. Any time we find the sum not being close to one we should be suspicious of the data. This analysis also gives the progression of the vibration-rotation matrix element, which can be used to determine Hermann-Wallis factors. We have performed this check on some of the HITRAN91 data. In particular, we have looked at CO_2,, CO, H_2O, HF, HCl, and N_2. The sum on all connecting states depends on the molecule, for example for CO_2 for a particular J" we must sum on the P, Q, and R transitions from that level. For CO, HF,and HCl only P and R branches enter into the sum; for water vapor the selection rules for an asymmetric rotor must be used.

From the following relationship,

$$\sum_{M,\,M'} |R_{(nJM)(n'JM')}|^2 = \sum_{M,\,M'} |R_{(n'JM')(nJM)}|^2 \quad , \tag{73}$$

one can show that $d_\eta * R_{\eta\eta'} = d_{\eta'} * R_{\eta'\eta}$. Thus, for a particular vibrational band if one has the value of the reduced dipole matrix element from state nJM to n'J'M' and the value for n'J'M' to nJM is needed one can uses the formula

$$\langle J'||\mu||J\rangle^2 = \frac{d_J}{d_{J'}} \langle J||\mu||J'\rangle^2 \quad . \tag{74}$$

This is necessary when applying the sum rule to water vapor for example. It is also useful for other molecules when all the $R_{\eta\eta'}$'s are not available. Table 8 gives the results for some of the checks done using Eq. (72)

From these studies, we have found a typographical error for the R2 line of the fundamental of HF (noted above). Comparing the line intensities we found a value of 2.26 $x10^{18}$ from the 1986 database and 4.196 $x10^{18}$ from the 1991 databases After discussing this with R. Tipping, he stated that the HF data was created by hand hence typos were a possibility. Tipping thinks that the 4 should be a 2, i.e. the 1991 value should be 2.196 $x10^{18}$. He will check this and during his visit to the Geophysics Laboratory in July we will correct the data. An interesting problem was found in the HCl data one of the $R_{\eta\eta'}$ had an exponent of -61. These numbers were created by the FORTRAN program TR-MOM with no hand operations. As a check the HCl data was extracted and TR-MOM run again on this and all the data was correct. Thus we are not certain at this time how the E-61 occurred on the database. We will consider writing a general program to check the $R_{\eta\eta'}$ on the database.

Table 8. Sum Rule Checks of $R_{\eta\eta'}$

Molecule	$\|M_{0,0}\|^2 \times 10^{36}$	J"	$\sum_{J'} R^2_{\eta,Jn'J'} \frac{1}{\|M_{0,0}\|^2}$
CO	0.0118	1	1.0003
(1←0)		2	1.0004
fundamental		7	1.0009
		11	1.0014
		14	1.0020
		19	1.0031
CO_2	0.0330	4	1.0000
		10	1.0000
		16	1.0000
		18	1.0000
HCl	0.005188	1	1.00058
(1←0)		6	1.01099
fundamental		15	1.06361
HF	0.009428	1	1.0017
(1←0)		2	1.45948 ***
fundamental		3	1.01050
		4	1 01803
		5	1.02630
		6	1.03670
		7	1.04868
		8	1.06216
H_2O	3.44121	2 2 1	1.008
(0←0)		1 1 0	1.000

*** Error in line intensity

7.0 1991 HITRAN WORKSHOP

The 1991 HITRAN workshop was held at the Geophysics Laboratory from June 13th to the 14th There were many interesting talks on both the status of the 1991 Edition of the database and on future needs and data. Below the final session entitled Summary, Review, and Recommendations is summarized, molecule by molecule.

H_2O Few comments about water vapor, V. M. Devi mentioned having some shift measurements.

CO_2 Both V. M. Devi and A. Barbe said that they had pressure shift measurements. A problem with the CO_2 halfwidths on the database (Rosenmann et. al.[80,81]) being too large was brought up. In general the halfwidths are needed to better than 5% uncertainty. Rothman mentioned the $R_{\eta\eta}$'s being fully implemented. J. Johns questioned the definition we used but when he found it is related to Hertzberg's[41] definition of the Einstein coefficient for induced absorption he said it was ok.

O_3 Not much said.

N_2O Toth will have new data soon, also pressure shifts for v3.

CO Not much said, L. Brown requested a copy of Tipping's final report on CO.

CH_4 Discussion centered around the unassigned lines. L. Brown set the lower state energy to 300.555 whereas HITRAN has used a negative E" in the past. It was suggested to change Linda's values to negative numbers. M. A. H. Smith has some CH_3D data.

O_2 Need a complete revamping.

NO No comments.

SO_2 Update needed, A. Pine has v_1+v_3.

NO_2 Use data of Perrin et. al..

NH_3 Update with data of S. Urban. GEISA has data from Meudon with many unassigned lines. There are notation problems - not consistent.

HNO_3 No comments.

OH Goorvitch, Chackerian data. J. Selby questioned A. Goldman on the intensities being off by a factor of 2 to 6.

Hydrogen These are fine.

Halides

ClO Randy May to measure Hermann-Wallis factors. K. Chance said it would be nice to have cross ladder transitions, A. Goldman mentioned he may have them.

HCN Possibly an update.

OCS N. Husson has data.

H_2CO	No comments.
H_2O_2	Questions on the Hillman data, J. Johns has made measurements, A. Perrin also has data.
C_2H_2	No Comments.
N_2	No Comments.
PH_3	New data available from Tarrago.
SF_6	No comments.
HCOOH	No Comments.
H_2S	No Comments.

J. Selby commented on TIPS. He would like to see the high temperature partition sums improved, especially from 2000-3000K.
C. Benner commented on reference and error codes. They are extremely useful and should always be implemented.
S. Clough wanted to know when the next edition would be distributed. This created a discussion which indicated that the scientific community wants yearly updates if possible.

Other comments dealt with the addition of coupling coefficients to the database in the future. No consensus was arrived at. Here I would like to add some comments. At this phase of evolution of the database I think it might be useful to add fields for the temperature exponent for self-broadening, as well as error and reference codes for self-broadening and shift parameters. However I do not believe that adding coupling coefficients to the database would be wise. All the spectroscopic data that are presently on the database are *fixed by nature*. By this I mean that if several laboratories make measurements or calculations are made of the same quantity they should agree, i.e. there is <u>one</u> "God" given value, if you like. With the coupling coefficients there is a danger in that they are dependent on the model chosen. Even worse, within the model the coupling coefficients are determined via sum rules over a number of lines and when applied all the lines must be used or serious errors do occur as shown by L. Strow. It would be dangerous to mix these two types of data. I would suggest the inclusion of coupling coefficients and any other of this type of data as auxiliary files added to the third file of the database. The problem with adding this type of data to the main database is that users

take this data as "God" given and believe fully in results generated from them.

8.0 PAPERS AND PRESENTATIONS

8.1 The 43th Symposium on Molecular Spectroscopy, The Ohio State University, June 13-17, 1988.

Paper Te11, "Simplified Expression for the Total Internal Partition Sum as a Function of Temperature", with Robert Hawkins and Laurence S. Rothman.

8.2 1989 HITRAN Workshop

On June 8-9, 1989 a workshop on the HITRAN database was held at the Geophysical Laboratory at Hanscom Field. I gave two talks at the workshop, the first reviewed the collision broadened halfwidths and their temperature dependences and the second discussed the program SELECT along with some aspects of the database. The first talk emphasized the updates expected for the air-, and self-broadened halfwidths, the line shifts and the temperature exponent of the air-broadened halfwidth. The talk was to allow the audience to have an opportunity to request certain data to be put on for these fields, to bring to our attention data that was overlooked in our search, and to bring to our attention unpublished data. John Ballard of Rutherford Appleton Laboratory told us about some water vapor data of his student John Remedios which is unpublished and about some recently published NO data. John will send the data to us in July. Kelly Chance of Harvard-Smithsonian Center for Astrophysics has sent me his results for OH and will keep me informed of some ongoing determinations of broadening parameters for this molecule.

The second talk was on SELECT and presented the new features and options of the program. These include options for increased speed for searches, version labels that will link SELECT and HITRAN, output at temperatures other than the reference, 296 K, and more. The current error codes were shown and were discussed with the audience. This led to

the codes for the line intensity and the halfwidths being changed. The codes now follow the wavenumber form in that as the code number gets larger the accuracy of the data increases. It was also decided to keep the error codes for S and γ the same. The implementation of the reference code and methods for its use was also presented and input from the community requested.

8.3 Journal of Molecular Spectroscopy

R. R. Gamache, R. L. Hawkins, and L. S. Rothman, "Total Internal Partition Sums in the Temperature Range 70-3000 K: Atmospheric Linear Molecules," J. Mol. Spectrosc. **142**, 205-219 (1990).

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